PHOSPHORUS SOLUBILITY IN PADDY SOILS IN RELATION TO RICE AND *AZOLLA* YIELDS

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INTRODUCTION

Rice yields are generally low in the subsistence farming systems of developing countries, because rice monoculture has depleted soils of nutrients. A survey of nutritional disorders of rice in Asia indicated areas where phosphorus is deficient for rice (Tanaka and Yoshida, 1970). For every ton of rice harvested, about 2.5 kg. of P is taken from the soil. High-yielding varieties can extract as much as 37.0 kg. of P per hectare (Sanchez, 1976). It is generally reported that soil P is more available to flooded rice than to upland rice. Increased solubility,leading to increased uptake, hastens soil depletion. To maintain or to improve yields, P from some source must be applied to replace P taken up by the crop. A reliable method of estimating P availability to rice and requirements of soils for phosphate fertilizer to maintain a given level of P and an understanding of the behavior of applied P should lead to efficient use of the fertilizer for paddy culture.

Freqently nitrogen is too low for optimum growth and yield of paddy rice. Substantial increases in yield require that additional N be introduced into the system. In many areas this cannot be accomplished with fertilizers. Azolla, an aquatic fern living in symbiosis with blue-green algae, is a fast growing green manure crop that may be useful in this respect. Under favorable conditions, it can biologically fix 3 kg. of atmospheric N per hectare per day (Watanabe et al.,

1977). Azolla, intercropped with paddy rice or incorporated into soil improved the grain yield of rice (Rains and Talley, 1978; Le Van Kan and Sobachkin, 1963). Solutions lacking in P severely reduce the growth and nitrogen accumulation of Azolla (Watanabe et. al., 1977). If Azolla is to be an effective source of supplementary nitrogen for the rice plant, the P status of paddy soils in relation to the growth of Azolla should be studied.

The objectives of this study are:

1) To develop techniques for determining the P sorption capacity of flooded soils.
2) To determine the characteristics of P sorption of some paddy soils of the tropics in relation to the yield of rice.
3) To investigate the use of P sorption curves for predicting the response of rice and Azolla to applied P in some Hawaii soils.

LITERATURE REVIEW

Chemistry of Submerged Soils

Studies of the availability of P to paddy rice are complicated because the chemistry of P in submerged soils is not well understood. For one thing, changes in soil Eh and pH as influenced by the moisture regime affect the availability of P.

The most important chemical difference between a submerged soil and a well-drained soil is that the submerged soil is in a reduced state. Except for the thin bright-colored(red or brown),oxidized layer at the surface(and sometimes an oxidized zone in the sub-soil), a submerged soil has a low oxidation reduction potential (or Eh). Reduction of a soil is a consequence of anaerobic respiration by soil bacteria. During anaerobic respiration, organic matter is oxidized and soil components are reduced.

Redox potential(Eh) is a quantitative measure of the tendency of a given system to oxidize or reduce susceptible substances. An Eh value is positive and high in a strongly oxidizing system;it is negative and low in a strongly reducing system. Although Eh reveals whether a soil is aerobic or anaerobic,it is unsatisfactory as a measure of oxygen concentration in soils and has little diagnostic value in rice culture(Ponnamperuma,1965;1972).

Usually when an aerobic soil is submerged,its pH decreases during the first few days,reaches a minimum,and then increases asymptotically to a fairly stable value of 6.7 to 7.2 a few

weeks later. The overall effect of submergence is to increase the pH of acid soils and to depress the pH of sodic and calcareous soils.

In submerged soils, the pH value profoundly influences hydroxide, carbonate, sulfide, phosphate, and silicate equilibria which, inturn, regulate the precipitation and dissolution of solids and the sorption and desorption of ions (Ponnamperuma, 1972).

Laboratory studies by Holford and Patrick (1979) confirmed that there is a strong interaction between changes in redox potential and changes in pH. Decreasing redox potential causes the reduction of ferric iron compounds while pH controls the dissolution and subsequent precipitation of the reduced compounds.

Availability of Phosphorus in Submerged Soils

The availability of soil P usually increases after soils are submerged (Ponnamperuma, 1964, 1972 and Patrick and Mahapatra, 1968). Shapiro (1958a, 1958b), and Chang and Chu (1959) reported that there was an increase in isotopically exchangeable P when soils were flooded. Chang and Jackson (1957) fractionated inorganic phosphates into the following forms: iron-bonded P, aluminum-bonded P, calcium-bonded P, reductant-soluble P and occluded P. While all forms of inorganic P are available to plants to a greater or lesser extent, iron-bonded P appears to be most readily available to paddy rice (Chang, 1965; Chu and Chang, 1966). Tyner and Davide (1962) believe that P availability in paddy soil is a function

of the magnitude and reactivity of the iron-bonded P fraction. Cholitkul and Tyner (1971) concluded that iron-bonded P and reductant-soluble P were the most abundant inorganic P fractions in paddy soils from Thailand. As an average these amount to 35% and 19% of total P. A stepwise regression analysis relating labile P, as determined by isotopic exchange, to several P fractions, indicated that iron-bonded P was the prime source of labile P. In acid soils, increased P availability is associated with decreased redox potential or increased ferrous iron suggesting a role of iron-bonded P (Ponnamperuma, 1964; Patrick and Mahapatra, 1968; Shapiro, 1958). Shapiro (1958) reported that P availability was considerably enhanced in calcareous soils and muck soils low in iron-bonded P as a result of flooding. He concluded that increased availability of soil P is mainly due to reduction, rather than hydrolysis. Sarangamath et. al. (1975) reported that water soluble P was more available to the rice plant than citrate-soluble P and insoluble P. Later, Sarangamath et. al. (1977) suggested that free hydrogen ions in acid soil systems favor the dissolution of citrate-soluble and insoluble P. Application of the two forms of P resulted in an increase in aluminum-bonded P and also moderate increase in 0.5 M $NaHCO_3$ extractable P and 0.03 N NH_4F + 0.025 N HCl extractable P, after 30 days of moist aerobic incubation. Such change was not observed in soils with a pH above 7.0.

Phosphorus Sorption Capacity of Submerged Soils

Soils under anaerobic conditions sorb P by the same mechanisms as under aerobic conditions. Patrick and Khalid (1974) observed that submerged soils released more P to soil solutions low in soluble P and sorbed more P from solutions high in soluble P than did aerated soils. Willet and Higgins (1978) reported that upon submergence acetate and oxalate extractable iron increased, enhancing P sorption capacity by the soils studied. Additions of organic matter initially increased the rate of formation of extractable iron, and P sorption capacity increased accordingly. More P was sorbed per unit Fe(oxalate extractable) under oxidized than reduced conditions. Khalid et al.(1977) suggested that a close relationship between P sorbed and oxalate extractable Fe under reduced conditions indicates that poorly crystallin and amorphous oxides and hydroxides of Fe play a primary role in P retention by flooded soils and sediments. Perhaps greater surface areas generated by transformation of oxyferric hydroxides to more reactive ferrous compounds may be responsible for greater P sorption under reduced conditions than under oxidized conditions.

Several investigators have reported that during 3 to 4 weeks following submergence, P in soil solutions that were not treated with P fertilizer first increased and then gradually declined (Hossner et al.,1973 ; Islam et al.,1973; Katyal, 1978). Such decline is believed to be due to the reprecipitation as iron and manganese-bonded P (Valencia,1962;Mahapatra

and Patrick,1969;Patrick and Mahapatra,1968). Holford and Patrick(1979) called attention to the uncertainties concerning the roles of ferrous phosphate precipitation and P adsorption in accounting for P retention in anaerobic soils. When P is added to a reduced system,its adsorption by newly formed ferrous iron and residual hydrous oxide phases and its precipitation by ferrous iron and calcium ions is influenced by the pH of the system. Khalid et al.(1977) reported that P sorption increased only in anaerobic soils whose pH rose to 6.4 or more upon submergence,apparently because ferrous hydroxide did not precipitate at lower pH values.

Soil pH values between 5.0 and 7.0, and Eh values of less than -200 mv were required to initiate substantial dissolution of iron-bonded P, while at soil pH values less than 5.0, dissolution commenced at Eh values as high as +200 mv (Williams and Patrick,1973). In attempting to identify the separate roles of Eh and pH, Holford et al.(1979)observed that at all pH values,bringing the soil to a reduced state increased the concentration of native P in solution. At pH 6.5 this was caused by an increase in labile P due to a release of occluded P. At pH 5.0 and pH 8.0 such increase was caused by a decrease in phosphate bonding energy.

Soil Phosphorus Tests

There are numerous methods of determining available P in soils. Basically these tests can be divided in two groups: those involving extraction procedures,and those involving

equilibration procedures. Most of them have been developed primarily for upland soils. These soil tests generally fail when utilized for the estimation of P in flooded soils. Poor correlations between P test values and rice yields are obtained in the field and even in pot studies (Chang,1965).

Method for extracting phosphorus. An ideal extractant for plant-available P is one that extracts only the available pool of P in soils,or a proportional part of the available pool. The ideal extractant has not been formulated,nor is there any likelyhood that it will be. Among P extraction methods,those of Bray and Kurtz (1945),Olsen et al. (1954), or their modifications have been widely used in rice growing countries. The suitability of these methods for predicting the P status of soils has been reported in Taiwan (Chu and Chang,1960;Wang and Tseng,1962;Chang and Juo,1963;Wang,1965; and Lin et al.,1977),in India (Tamhane and Subbiah,1960;1962; Bhan and Shanker,1973;Gupta and Singh,1975), in the Philippines (DeDetta,1966;Samonte and Mamaril,1966;Layese and Tilo, 1970), in Thailand (Vajragupta et al.,1963;and Cholitkul and Tyner,1971),and in Japan (Komoto,1971;Shiga,1976;Miyake,1978). In all cases, the suitability of the methods were judged by the degree of correlation between P extracted and percentage of maximum yield attained or P uptake. Most methods of P extraction provide a good index of P availability if used on soils that are similar in all respects except P status. Layese and Tilo (1970) reported that Olsen's extractant

(0.5 M $NaHCO_3$) has a wide range of applicability to paddy soils,than either the Bray II (0.1 N HCl + 0.03 N NH_4F) or the modified Truog (0.02 N H_2SO_4) methods. On the basis of correlation studies made on long term pot culture using the main paddy soils of Taiwan, Wang (1965) concluded that the following extractants were suitable for all soils tested: Bray I (0.025 N HCl + 0.03 N NH_4F), Saunder (0.1 N NaOH) and Olsen (0.5 M $NaHCO_3$). The Bray II extractant (0.1 N HCl + 0.03 N NH_4F) and Mechlich extractant (0.05 N HCl + 0.025 N H_2SO_4) were suitable only for strongly acidic soils such as latosols in which the phosphate chemistry is dominated by iron-bonnded P. Among the three suitable methods, the Bray I method was selected for routine testing because it is simple and quick. Gupta and Singh (1975) reported better correlation between isotopically exchangeable P and amount of P extracted by Olsen's method than by the Bray I method. This result suggests that Olsen's extractant would be the better method for estimateing the "available" pool of P in paddy soils.

Regression analysis of the sources of P extracted by the Bray I,Bray II and Olsen methods indicated that aluminum--bonded P,a minor P fraction,was the major source of P extracted (Cholitkul and Tyner,1971). Among extractants used for rapid assessment of available P,no single extractant was universally applicable(Bhan and Shanker,1973). But Olsen's method was more reliable than other methods in estimating P availability to rice plants. Semonte and Mamaril(1966) reported that the Bray II P test correlated best with absolute

grain yield of rice. He also reported that the Olsen's method correlated best with P uptake. Such results are difficult to reconcile and do little to instill confidence that the methods are measuring what they were supposed to measure. Lin and Chang(1977) reported that P uptake by rice plants grown in pot culture without drainage was highly related to soil iron-bonded P,but less so in field conditions. They suggested that P-test calibration equations should include the variables representing soil factors which affect the solubility of soil P and P uptake of the crop. Cholitkul and Tyner(1971) asserted that an extractant needs to be more specific for iron-bonded P when air dried samples are used. Many extractants do not extract much iron-bonded P. None of the soil extractants in common use detects reductant-soluble P,which may become available when soils are flooded.

The critical question is, does a soil P test made on a soil sample which is aerobic(Eh value of about 650 mv) apply to anaerobic soil conditions that are typical for rice? To account for the increased P availability generally observed when soils are flooded, Ekpete(1975) flooded soils samples before extracting the P. He compared five extraction methods (Bray I, Bray II, Truog, EDTA,and Olsen) and observed that all of them extracted more P from soil samples that were preflooded for six weeks, than from air-dry samples. The Olsen procedure extracted more P from both preflooded and air-dry soils. He suggested that Olsen's method can be used on air-dry samples to determine P availability in paddy soils.

Gupta and Singh(1975) suggested recalibration of the tests to allow for the increased amount of P in labile form that is associated with a shift from an aerobic to an anaerobic condition.

Shapiro(1958) demonstrated that the effect of flooding soils to which organic matter had been added,as compared with flooding with no organic matter added, was to increase the availability of iron-bonded P to rice plants much more than aluminum-bonded P. DeDatta et al. (1966) observed that flooding four soils for 3.5 months increased extractable P by 2.5 to 15 times. Shiga(1976) obtained a consistant increase in the Bray II extractable P with time of flooding. He investigated peat and volcanic ash soils. Miyake(1978) modified Olsen's method by using EDTA in combination with 0.5 M $NaHCO_3$ to keep Fe in a soluble form,hence retarding P re-adsorption by iron hydroxide during extraction. The method he proposed was suitable for a wide range of soils(18) from Japan and Indonesia.

Method of equilibration. The problem of estimating the availability of P in submerged soils (soils suited for rice cultivation) is quite different from that for well-drained, aerated soils. A wet soil has a greater cross-sectional area filled with water through which ions can diffuse than a dry soil has (Viets,1967). The rate of ion diffusion in a soil is directly related to soil water content through its effects on tortuosity of the diffusion path and the cross-sectional

area containing water (Barber,1962). Lipps and Fox (1956) reported that low moisture tension, i.e. high water content, increased the mobility of P. Olsen et al. (1961) predicted that P uptake by a plant should be a linear function of the moisture content of a soil. The factors controlling P uptake (by plants) in relation to soil moisture tension were: thickness of moisture films, length of diffusion path, degree of hydration and root interception. Plant uptake of P at constant moisture tension from soils differing in texture and soluble P was a linear function of solution P concentration.

Fox and Searle(1978) stated that the immediate source of P for the plant growing in soil is the P in the soil solution. Furthermore, a close relationship exists between P remaining in solution and P sorbed by the soil;when P is added to soils P remaining in solution varies directly with the quantity of P sorbed by the soil. This information can be used to plot a P sorption curve as outlined by Fox and Kamprath(1970). The fertilizer requirement for a given crop can be estimated from the amount of P sorbed to establish the critical level of P in solution for that crop. Fox et al.(1974) reported that corn growing on two soils which had different P sorption capacities had the same requirement for P in solution. Vander Zagg et al. (1979) concluded that P sorption curves were adequate means for making predictions about P fertilizer requirement of soils having different P sorption characteristics.

No work has been published using P sorption curves to predict P requirement for paddy soils. One of the reasons is

that it is cumbersome to incorporate the effects of flooding into soil test procedures. A step in the right direction has been indicated by Shahi(1975) and Hossner and his co-workers (1973). Shahi(1975) suggested that water-soluble P in soils is the best source of P for rice plants when P is applied after flooding. Hossner et al.(1973) monitored the P concentration in solution from soils during the vegetative growth of rice growing in pots and reported that dry matter yields 90% or more of the maximum were obtained when the average P values were 0.1 ppm or higher. Fox and de la Pẽna (unpublished data) observed no significant yields response of lowland taro to P applied when P in soil solution extracted from the reduced zone was 0.02 ppm.

In summary, a soil test for available P in flooded soils should be a test that is specific for iron-bonded P and water-soluble P. It should take into account the effects of flooding . For practical purposes it should have the ability to predict P fertilizer requirement for a given relative yield. Predictions based on P sorption curves after equilibrating the soil under reduced condition is a logical method; however there are numerous analytical problems and the procedure is cumbersome.

MATERIAL AND METHODS

Anaerobic P Sorption

The following material describes the procedure adopted for determing P sorption curves under anaerobic conditions. Justifications for adoptions of certain procedures are discussed in the section on "Results and Discussion" of this thesis.

In a 50 ml screw-top centrifuge tube, 3.0 g of oven-dry equivalent soil was incubated for two weeks in 30 ml(17 ml if P solution was to be added) of distilled deionized water (boiled for one hour) containing 0.01 M $CaCl_2$ and 0.01 g of finely ground rice straw. A medium size,sleeved,rubber septum (with stopper-end removed) was used as an airtight cap. To purge the system with nitrogen gas,suction was applied for 3 minutes with a needle pierced through the septum and connected to the laboratory vacuum outlet. The centrifuge tube was intermittently tapped to help free the air bubbles entrapped in the soil. A second needle, connected to a compressed nitrogen gas supply,was pierced through the septum. Simultaneous action of vacuum and nitrogen gas flow was allowed to continue for about 3 minutes. The vacuum was then disconnected. Thirty seconds or more later the nitrogen gas inlet was disconnected. The tube was shaken on a horizontal shaker for 30 minutes to insure proper mixing of soil and rice straw. After two weeks of incubation in the dark at room temperature, 3 ml of different standard concentrations of P as monobasic

calcium phosphate were injected into the tubes with a syringe. The tubes were shaken twice a day for 30 minutes during a 6-day incubation after which they were centrifuged for 20 minutes at 10,000 rpm. To prevent the rubber septum from plunging into the tube during centrifugation, the tubes were pressurized at slightly above one atmosphere by injecting 10 to 20 ml of nitrogen gas into them before centrifuging.

To determine P in solution,a 10 ml aliquot of supernatant solution was removed with a syringe having a long needle and placed in a plastic vial containing 2 ml of Murphy and Riley's (1962) reagent B and 0.5 ml of water. A second 10 ml aliquot was removed and placed in a vial containing 2.5 ml of 2 N H_2SO_4 for the determination of optical density of the supernatant solution. The difference between the optical density of a supernatant solution with the reagent B and that of a supernatant solution with 2 N H_2SO_4 was the net optical density of the blue color which was developed due to the presence of P. The space created by the removal of the two 10 ml samples was filled with nitrogen gas. Phosphorus in solution was plotted against the calculated quantity of P sorbed by the reduced soil. Iron concentration of the supernatant solution was determined using an atomic adsorption spectrophotometer. The pH of the supernatant solution was measured immediately after the remaining solution was poured out of the tubes.

Greenhouse Experiment

A greenhouse experiment was conducted to investigate the use of P sorption curves for predicting the response of rice and Azolla to applied P fertilizer.

Rice was grown in four Hawaii soils having different P sorption capacities and native P status. The classification and chemical analyses of these soils are presented in Table 1. Triplicate of 2.5 gallon plastic pots containing the equivalent of 5 kg of oven-dry soil were flooded three weeks prior to puddling and fertilizer application.

A filter device with provision for extracting soil solution was buried near the bottom of each pot (Fig.1). This home-made filtering device consists of an upside-down 50 ml plastic vial,with big holes bored on its wall,wrapped with two layers of silk screen No. 17 (the finest mesh available). The soil solution can penetrate into the vial only through the silk screen. Two plastic tubes were tight-fitted on to the top of the upside-down vial(bottom of the vial). One tube functions as a nitrogen gas intake to displace soil solution and to maintain a reducing atmosphere. The other tube,which protrudes further into the vial,serves as soil solution delivery tube.

Phosphorus (as $Ca(HP_2O_4)_2.H_2O$) and potassium (as KCl) were applied at the time of puddling. The amounts of P applied in each treatment to each soil are presented in Table 2. The selection of these P levels is based on the P sorption curves developed under aerobic conditions(Fig. 2) and the

Table 1: Chemical analyses of four soils used in the greenhouse experiment.

Soils	P desorbed		Extractable P[1]	P sorbed at 0.2 ppm P in solution		Free iron	Organic matter	pH	
	Aerobic	Anaerobic		Aerobic	Anaerobic			Soil paste	Soil solution[2]
	ppm					%			
Hanalei I	0.010	0.020	18.0	480	340	2.33	1.79	4.7	6.6
Hanalei II	0.021	0.023	55.8	340	450	8.40	2.28	5.5	6.2
Kaloko	0.004	0.006	11.5	185	260	3.43	1.09	6.8	6.8
Lualualei	0.470	0.985	32.5	-10	-50	1.55	1.96	6.9	6.7

1 Olsen et al. (1954)

2 Anaerobically equilibrated solution.

Soil classification:

Hanalei Soils: Fine, mixed, isohyperthermic Typic Tropaquept.

Kaloko Soil: Fine, carbonatic, isohyperthermic Typic Haplaquoll.

Lualualei Soil: Very fine montmorillonitic, isohypertermic Typic Chromostert.

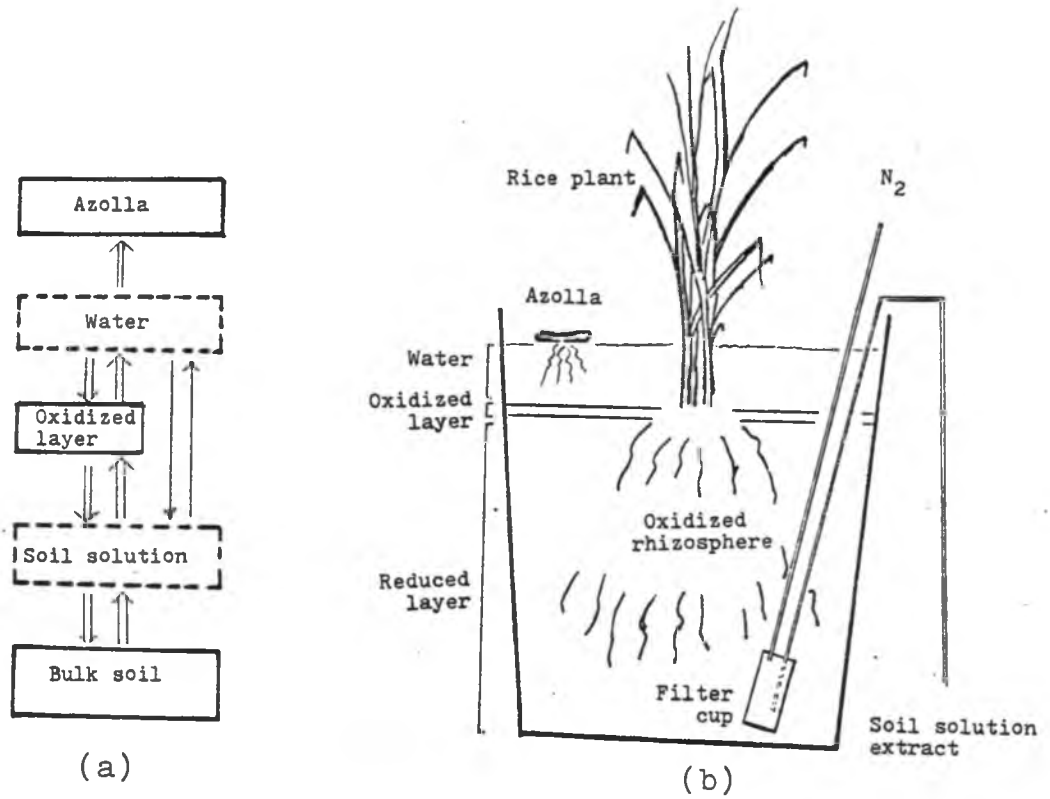

Fig. 1: (a) Diffusion path of water soluble P.
(b) Position of a filter cup in pots.

Table 2: Phosphorus treatment levels, amounts of P added and estimated P in solution of four soils used in a greenhouse study.

Soils	P treatment levels	P added	P intented
		ppm	
Hanlei I	0	0	0.010
	1	4	0.011
	2	13	0.012
	3	44	0.018
	4	87	0.030
Hanalei II	0	0	0.021
	1	4	0.022
	2	22	0.027
	3	65	0.040
Kaloko	0	0	0.004
	1	2	0.004
	2	4	0.004
	3	13	0.005
	4	22	0.007
	5	65	0.023
Lualualei	0	0	0.470
	1	2	0.600
	2	4	0.700
	3	13	1.000
	4	44	4.750

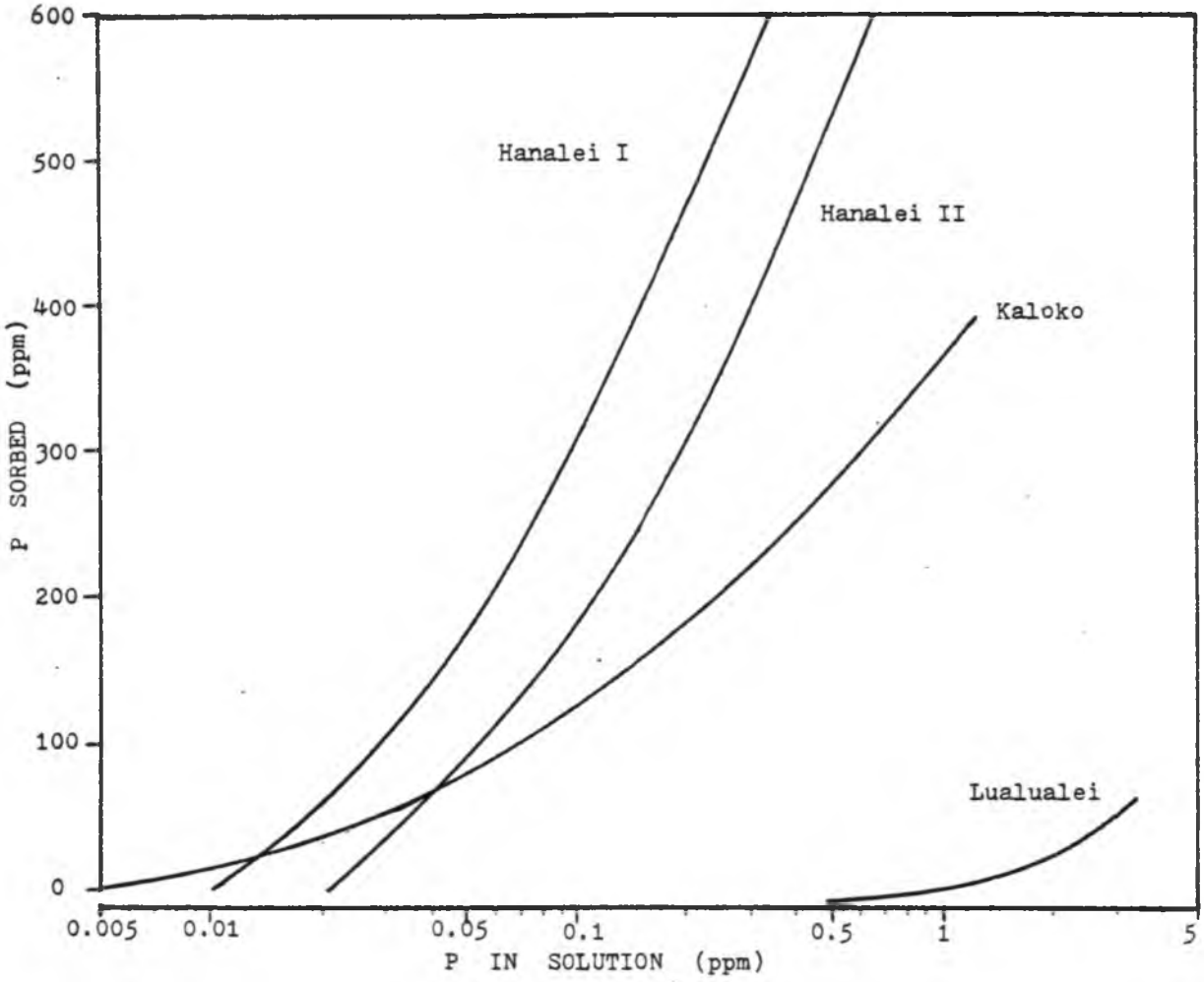

Fig. 2: Phosphorus sorption curves under aerobic conditions.

native P in soil solution extracted from the reduced zone. Based on the results of Hossner et al.(1973),attempts were made to establish 0.1 ppm P as a center point of intended P in soil solution among treatments. A blanket application of 300 kg/ha of K (as KCl) was applied. Four two-week old seedlings were transplanted in each pot. A total of 400 kg of N/ha (as $CO(NH_2)_2$) was applied in three split-doses: 50% at transplanting,25% at tillering, and 25% one week before panicle initiation. The pots were arranged in a split--plot design (soils being the main plot and P treatments being the sub-plot). All pots were rotated once every two weeks.

Changes in the P concentration in the soil solution of the reduced zone were monitored weekly during the early stage of growth and less frequently as the rice plant matured. Soil solution was extracted from the bottom of the pot using the filtering device described previously. To obtain fresh soil solution, the filtering device was drained 24 hours before sampling time. About 30 ml of the filtrate was siphoned(or pumped with a syringe) into a plastic vial containing one drop of concentrated HCl to maintain reduced conditions. Appropriate aliquots were immediately taken for the determination of P using the molybdate blue method as described by Murphy and Riley(1962).

To minimize to the extent possible the competition for P between Azolla and rice,ten fronds of Azolla filiculoides were introduced into each pot three weeks after panicle initiation (or 9 weeks after transplanting) of the rice plant. Phosphorus

concentration in free surface solution was determined prior to and 3 weeks after the introduction of Azolla. After seven weeks of growth, the Azolla were collected, washed and oven-dried, and dry weight determined. After wet digestion of the plant material, P content in Azolla was determined, About ten flag leaves of the rice plants were sampled for P determination. Sixteen weeks after transplanting, rice grain and straw were harvested and dry weight and P contents determined.

After harvesting the rice and Azolla the pots were drained and soil materials were sampled in the oxidized layer (top 2 to 5 mm), and in the reduced zone (center of the pot). The samples were stored under water in an airtight plastic vial in a refrigerator until Olsen extractable P and anaerobically desorbed P could be determined.

Field Experiments

To estimate the external P requirements of rice grown in the field, soil samples from control plots (no P) of P experiments on rice were collected, together with yield data from cooperaters in several countries (yield data were not obtained in all cases). Phosphorus sorption capacities of these soils under aerobic conditions (Fox and Kamprath,1970) and under anaerobic conditions (described in this thesis), and extractable P (Olsen et al.,1954) were determined and plotted against percentage of the maximum grain yield of rice.

Chemical Analyses of Some Paddy Soils

To identify some of the soil properties that may influence the P sorption characteristics of some paddy soils, several chemical analyses were carried out on 46 soil samples from 8 rice producing countries. These analyses include: organic matter content as described by Walkley and Black (1934); free iron oxides content as described by Kilmer (1960); pH of soil paste from air-dry soil samples; iron concentration and pH of anaerobically equilibrated supernatant solution; aerobically and anaerobically desorbed P; extractable P as described by Olsen et al. (1954); and amount of P sorbed at 0.2 ppm under aerobic and anaerobic conditions. Soil properties that influence P sorption characteristics of paddy soils were identified based on the degree of correlation between the soil property involved and the amount of P sorbed at 0.2 ppm P in solution.

RESULTS AND DISCUSSION

Requirements for Developing P Sorption Curves Under Anaerobic Conditions

Procedures for determining P sorption curves are well established for soils under aerobic conditions. However, there is no widely accepted procedure for developing P sorption curves for soils under anaerobic conditions. The material which follows describes some of the requirements for developing P sorption curves that may be appropriate for submerged soils, some of the problems encountered in developing a method, and some of the results obtained with the method. Details of the method itself can be found in the section on "Material and Methods" of this thesis.

An airtight system was required to attain anaerobic conditions for equilibrating soil and P solutions. One of the mechanical problems encountered was the lack of an airtight cap for the centrifuge tubes that would permit adding and withdrawing solutions from the tubes without introducing atmospheric oxygen into the tubes. To maintain anaerobic conditions during and after centrifugation, these caps must withstand high centrifugal forces. Two devices were developed to satisfy these conditions. One device was a centrifuge tube with a polypropylene screw cap. A hole was bored onto the cap and a rubber septum glued on, plugging the hole. The second device was a centrifuge tube and a medium size sleeved--rubber septum with the stopper-end removed. The sleeve was

inverted over the opening of the centrifuge tube. Clear supernatant solutions were obtained by centrifuging for 20 minutes at 10,000 rpm. Both the modified cap and the rubber septum withstood this treatment.

An airtight system which contains soil, P solution, and nitrogen gas is not necessarily anaerobic. Soil materials and P solutions contain some adsorbed and dissolved oxygen. Preliminary studies were carried out to find the trend of the effects of added organic matter (rice straw) on the rate of depletion of oxygen by soil micro-organisms.

Forty six paddy soil samples which were collected from several rice producing countries were incubated in an airtight system flushed with nitrogen gas. After two weeks of incubation, rings of reddish precipitate were observed on the inner wall of all of the tubes. The amounts of precipitate and their distance from the soil-solution interface differed among soils. In samples where 0.3%(soil dry weight basis) rice straw was added, the reddish ring occurs further away from the soil-solution interface as compared with when no rice straw was added (Fig. 3). However ,the addition of rice straw did not seem to affect the amount of reddish precipitates. No chemical analyses were made either to identify or to quantify the reddish precipitates.

It is highly probable that the reddish substance was precipitated ferric iron (Fe(III)). Ferric iron is not water soluble whereas ferrous iron(Fe(II)) is. Water insoluble

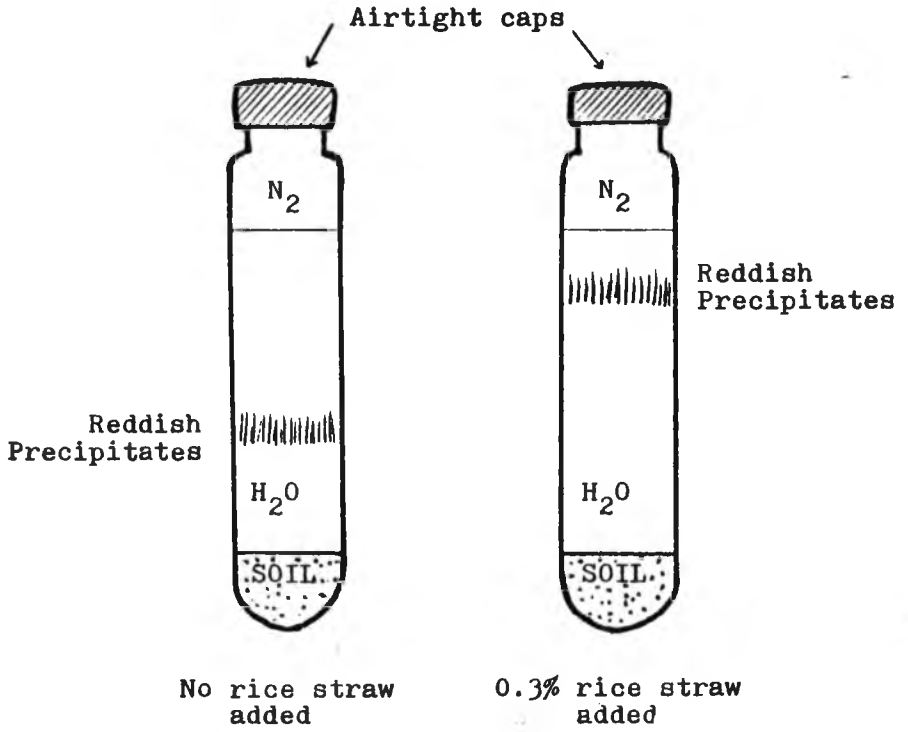

Fig. 3: Effect of rice straw on the position of reddish precipitates in incubation tubes.

ferric iron from aerated soil may have been reduced to soluble ferrous iron by microbial respiration and later reoxidized to ferric iron only when coming in contact with oxygen. The only obvious explanation for the reddish precipitates is that ferrous iron was reoxidized to ferric iron when coming in contact with dissolved oxygen in the solution used to suspend soil material. The addition of rice straw as a source of energy probably enhanced microbial activities and depleted dissolvedoxygen at a higher rate than when no rice straw was added pushing the reddish ring of precipitates further away from the soil-solution interface.

To minimize the introduction of dissolved oxygen into the samples to the extent possible, boiled water was used for preparing soil suspensions for equilibration. For the purpose of this discussion water boiled for one hour was considered to be oxygen free;unboiled water was considered to be oxygenated.

Further preliminary studies were carried out to find the trend of the effects of dissolved oxygen on P sorption capacities of three paddy soils. The results showed that less P remained in solution when oxygenated water was used in the equilibration as compared with when oxygen-free water was used(Fig.4). Also more Fe was found in the supernatant solution when oxygen-free water was used (Table 3). Oxygen in the water may have oxidized Fe(II) to Fe(III) causing it to precipitate and therefore enhanced P sorption by the soils,or the lack of oxygen may have hastened the reduction process,thus solubilizing P. Such findings were consistant with results

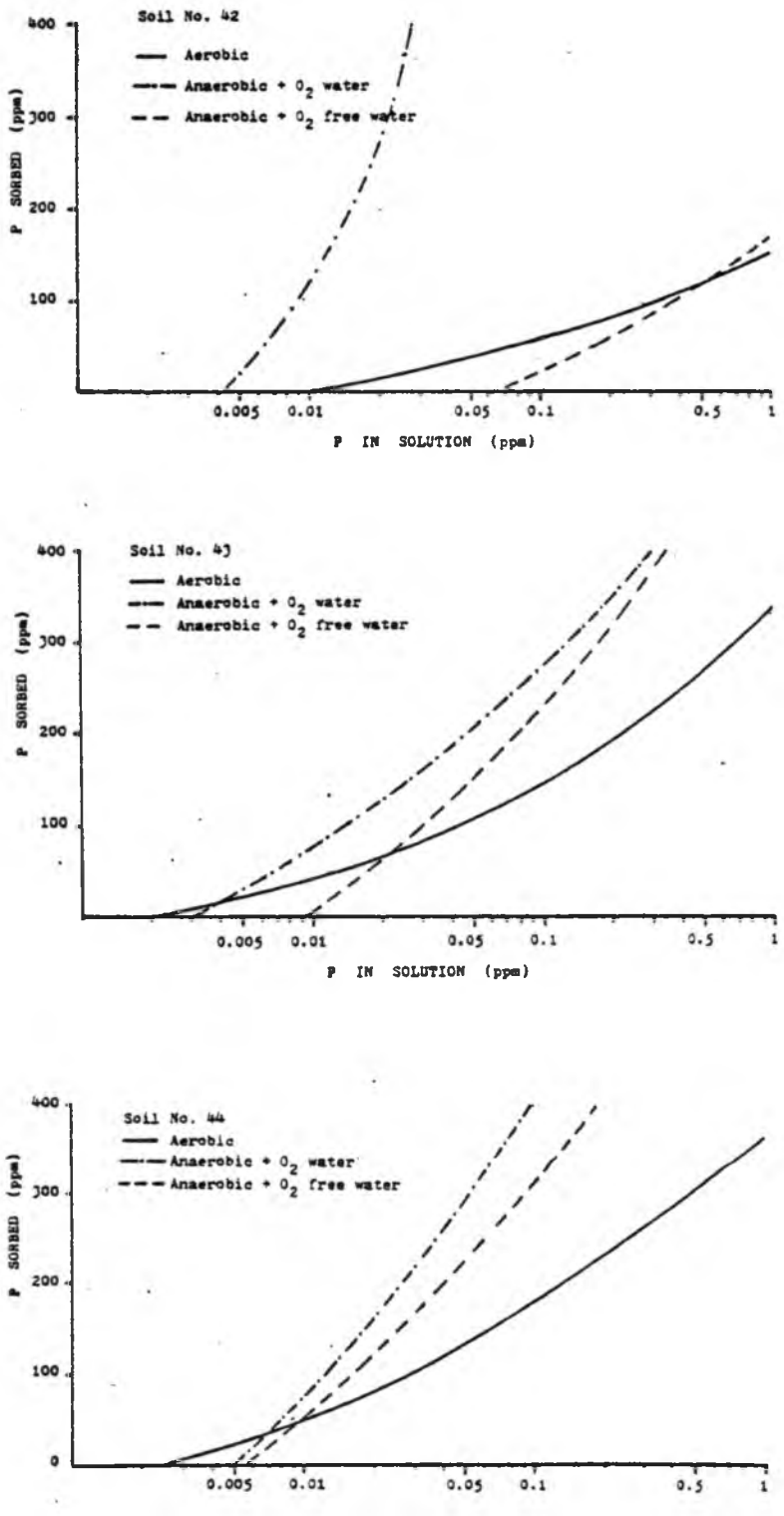

Fig. 4: Effects of dissolved oxygen on P sorption capacity of three paddy soils

Table 3: Effects of boiled and unboiled water on Fe solubility under anaerobic conditions.

Soil No.	ppm Fe	
	Boiled H_2O	Unboiled H_2O
42	22.5	9.1
43	17.3	17.1
44	13.7	3.3

of previous studies; Patrick and Mahapatra(1968) stated that increased solubility of P and Fe(II) were associated with low redox potential values,i.e. lack of oxygen. However,in this study,it is surprising to see so much effect of the dissolved oxygen after an extended period of incubation(3 weeks). Takai et al.,(1956) detected no oxygen one day after three soils were submerged. The wide ratio of soil to solution(1:10) in the procedure utilized here probably accentuated the effects of oxygenated water on the solubility of P and Fe. Thus freshly-boiled distilled water was used in the standard procedure of anaerobic equilibration even though the reason why it was required is not fully understood.

Soil test values are meaningless if they cannot be reproduced. Table 4 shows duplicate values of anaerobic P sorption by 5 soils. The degree of reproducibility (or similarity between replicates) of P in solution varied between soils. Phosphorus remaining in solution was difficult to reproduce in many samples (see for example, sample No.23,a soil from Taiwan in Fig. 5). The different degrees of reproducibility in different soils indicated that the problem was probably soil-related rather than a mechanical problem. Data from 25 samples of the 46 paddy soils were difficult to reproduce. Among them,23 samples (out of 30) were from Taiwan,and 2 samples (out of 2) were from Bangladesh. Since no information on these soils was available, other than the information presented in Table 5,it is only possible to suggest that past management may have enhanced the heterogeneity of the soil

Table 4: Replicate values of P, Fe and pH of soil solution under anaerobic conditions.

Soil samples	ppm P added	P in solution ppm		Fe in solution ppm		pH of solution	
		R_1	R_2	R_1	R_2	R_1	R_2
23	0	0.496	0.865	16.24	30.04	6.3	6.5
	50	0.034	1.584	0.08	25.24	----	----
	100	0.060	0.881	0.00	19.43	----	----
	200	1.134	1.196	20.89	18.30	----	----
33	0	0.009	0.012	30.63	32.19	6.7	6.7
	50	0.043	0.046	27.81	35.81	6.7	6.7
	100	0.159	0.116	-----	31.75	6.7	6.7
	200	0.614	0.613	35.50	37.00	6.7	6.7
36	0	0.270	0.221	63.38	28.31	6.7	6.7
	50	0.433	0.408	43.13	44.25	6.7	6.7
	100	0.493	0.448	30.38	25.31	6.6	6.7
	200	0.984	0.971	28.13	29.06	6.7	6.7
37	0	0.001	0.001	0.00	0.00	4.7	4.5
	50	0.005	0.005	0.00	0.00	4.4	4.4
	100	0.013	0.014	0.00	0.00	4.4	4.4
	400	0.496	0.459	0.00	0.00	4.3	4.3
40	0	0.000	0.000	0.00	0.00	5.0	4.7
	100	0.015	0.019	0.00	0.00	4.6	4.5
	200	0.080	1.209	0.00	0.00	4.5	4.5
	400	0.746	0.984	0.00	0.00	4.5	4.4

R_x : Replicates

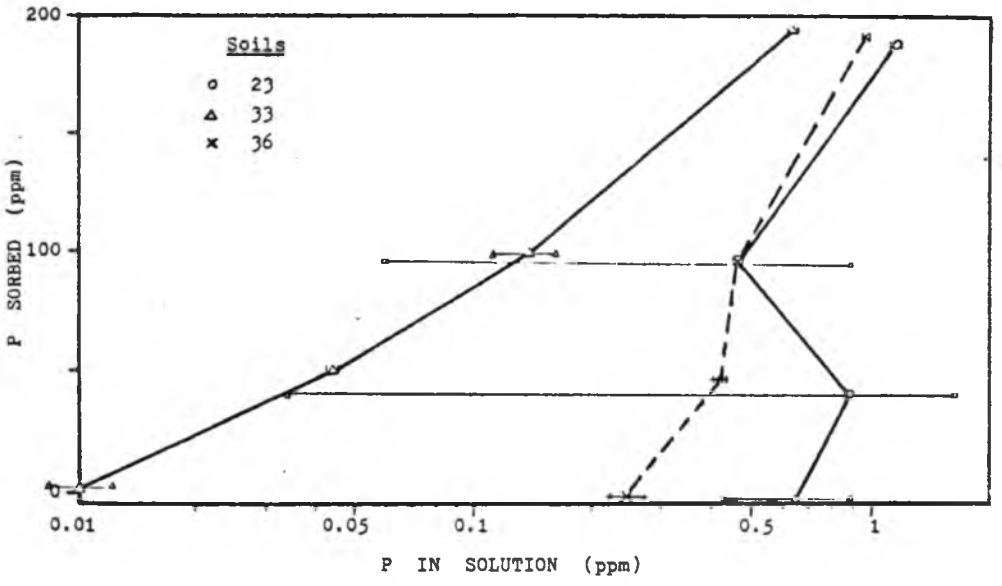

Fig. 5: P sorption capacities of three paddy soils under anaerobic conditions. The horizontal bars represent variation between two replicates.

Table 5: Chemical analyses of paddy soils

Soil #	P Desorbed (ppm)		P sorbed at 0.2 ppm P in solution		Olsen P	Org. Mat. (%)	Fe[2] (%)	Fe in solu.[1] (ppm)	pH		Location[3] (country)
	Anaero.	Aero.	Anaero.	Aero.					Soil paste	Soil solu.[1]	
1	0.0037	0.0090	150	75	1.6	0.56	0.64	2.89	5.2	6.1	Ta
2	0.0150	0.0063	90	30	10.1	0.74	0.24	3.58	5.2	6.3	Ta
3	0.0037	0.0040	250	161	6.7	0.63	0.31	1.81	5.4	6.4	Ta
4	0.0050	0.0030	415	95	6.1	0.42	0.68	11.29	5.0	6.0	Ta
5	0.0113	0.0050	138	38	10.3	0.56	0.93	4.10	4.8	5.8	Ta
6	0.0088	0.0030	205	56	8.8	0.77	0.89	6.58	5.7	6.3	Ta
7	0.0088	0.0063	88	45	8.5	0.63	0.66	2.26	5.3	6.3	Ta
8	2.0490	0.0100	0	42	10.1	0.77	0.89	33.64	5.3	6.4	Ta
9	0.0088	0.0190	67	42	29.7	0.56	1.02	9.00	4.6	6.0	Ta
10	0.2800	0.0050	0	75	5.6	0.77	1.36	99.88	4.9	6.3	Ta
11	0.0013	0.0050	180	75	7.6	0.46	1.00	1.99	6.0	6.5	Ta
12	0.0088	0.0063	140	75	12.5	0.70	1.44	9.24	5.6	6.5	Ta
13	0.5225	0.008	145	80	14.9	0.67	0.46	89.65	4.9	6.3	Ta
14	0.1337	0.0063	---	20	12.0	0.60	0.24	20.81	5.0	6.2	Ta
15	5.5120	0.0280	0	7	42.5	0.74	0.31	97.08	5.0	6.1	Ta
16	0.0162	0.0100	195	45	9.5	0.70	0.38	1.29	7.5	6.9	Ta
17	0.6737	0.0430	---	20	19.8	0.84	0.93	8.24	7.3	7.0	Ta
18	0.6075	0.0480	---	32	26.4	0.77	0.82	6.08	7.4	7.0	Ta
19	0.0600	0.0150	---	80	12.0	0.84	0.66	4.55	7.9	7.0	Ta
20	0.0038	0.0140	---	45	11.6	0.74	0.89	0.02	7.5	7.0	Ta
21	0.0338	0.0050	---	145	9.5	0.95	1.02	4.62	5.4	6.4	Ta
22	0.0013	0.0063	---	125	23.5	0.70	1.36	0.48	5.1	6.2	Ta
23	0.0550	0.0150	---	78	10.7	0.00	1.00	15.03	5.5	6.2	Ta
24	0.6185	0.0400	0	31	29.1	0.88	1.44	10.55	7.6	7.0	Ta
25	0.1050	0.0200	---	25	35.0	0.67	0.86	33.75	4.7	6.0	Ta
26	0.5890	0.0110	0	50	12.6	0.98	0.82	29.6	5.6	6.6	Ta
27	0.0150	0.0090	---	55	10.0	0.70	0.85	8.13	5.9	6.3	Ta
28	0.0075	0.0140	---	50	17.7	0.70	0.79	0.00	5.6	6.3	Ta
29	0.7740	0.0440	0	26	28.0	0.95	0.62	3.10	7.6	5.4	Ta
30	0.0063	0.0100	100	53	11.1	0.74	0.63	0.40	6.8	6.7	Ta
31	0.0030	0.0050	480	1240	2.6	1.30	4.86	16.68	5.5	6.4	Id
32	0.0040	0.0040	600	900	8.4	1.44	4.00	27.49	4.8	5.9	Si
33	0.0040	0.0020	280	180	4.7	0.49	1.23	8.12	6.7	6.3	Ba
34	0.0080	0.0040	200	275	10.3	1.54	1.23	9.35	4.7	6.5	In
35	0.0075	0.0025	180	130	11.3	0.56	1.75	3.34	7.2	6.9	In
36	0.0100	0.0080	300	210	25.2	0.63	1.61	22.8	5.4	6.4	Ba
37	0.0050	0.0020	270	190	2.4	0.60	0.93	0.11	4.4	4.4	Th
38	0.0480	0.0150	60	115	15.4	0.53	1.34	4.51	7.8	7.1	In
39	0.0050	0.0025	275	270	3.0	0.81	0.72	0.19	4.4	4.2	Th
40	0.0020	0.0050	430	110	3.4	0.77	1.55	0.02	4.4	4.5	Th
41	0.0012	0.0050	430	230	2.7	1.12	0.66	0.01	4.1	4.1	Th
42	0.0575	0.0100	230	170	10.3	0.46	1.34	22.48	5.4	6.7	La
43	0.0940	0.0020	330	200	8.2	0.88	1.08	17.25	5.2	5.6	Th
44	0.0560	0.0250	390	230	8.5	0.60	1.97	13.70	4.6	5.6	Th
45	0.0050	0.0020	520	450	6.1	2.14	1.58	116.28	4.6	6.2	Ma
46	0.0000	0.0020	230	210	2.5	0.81	1.56	0.48	4.6	5.1	Ma

1 Determined from anaerobically equilibrated solution.

2 Free iron (sodium dithionite extractable Fe).

3 Ba - Bangladesh; Id - Indonesia; In - India; La - Laos; Ma - Malaysia; Si - Sri Lanka
Ta - Taiwan; Th - Thailand

samples. Taiwan soils are usually intensively managed. Phosphates applied, coupled with seasonal wet and dry alternations, may have produced small pellets of residual P, around which Fe(III) and Mn(IV) oxides may have precipitated. This is a matter of speculation and is put forward because no other explanation is obvious.

An attempt was made to homogenize some of the samples by grinding them to pass through a 60-mesh sieve. The results, which are presented in Table 6, were still variable.

It is beyond the scope of this study to confidently identify the variables causing poor reproducibility in the P equilibration results. However, the following suggestions are given if, in the future, further efforts are made to perfect equilibration procedures: (1) flood a large sample in a glass jar in the dark for 2 to 3 weeks before small sub-samples are taken to be anaerobically equilibrated with P solutions; (2) retain the present procedure, but increase the soil to solution ratio from the present 1:10 to 1:2 ; (3) use glass centrifuge tubes instead of plastic tubes in order to minimize the possibility of oxygen diffusion through the plastic; (4) store the plastic tubes under nitrogen gas or periodically purge them with the same.

Phosphorus Sorption Capacities of Some Paddy Soils

The factors influencing P sorption capacities of upland soils under aerobic conditions have been well established (Fox and Searl, 1978). Soil mineralogy, which is related to

Table 6: Effects of 10 and 60 mesh sieved samples and additions of P on the solubility of P and Fe under anaerobic condition.

Soils	Treatments	P in solution (ppm)				Fe in solution (ppm)			
		R_1	R_2	R_3	X	R_1	R_2	R_3	X
15	*60 mesh seived No P added	0.233	1.680	1.990	1.301	20.3	41.0	44.9	35.4
	10 mesh sieved No P added	1.930	1.923	2.143	2.005	40.2	41.0	41.4	40.9
	10 mesh sieved 50 ppm P added	2.764	2.100	3.251	2.705	40.0	36.4	43.8	40.1
34	10 mesh sieved No P added	0.011	0.009	0.008	0.007	111.0	116.3	114.2	113.8
	10 mesh sieved 100 ppm P added	0.034	0.238	0.015	0.096	106.1	107.6	102.1	105.3
36	*60 mesh sieved No P added	0.044	0.106	0.034	0.061	40.3	51.1	37.7	43.0
	10 mesh sieved No P added	0.015	0.045	0.038	0.033	29.3	39.8	48.0	39.0
	10 mesh sieved 200 ppm P added	0.178	0.094	0.161	0.144	36.3	33.4	43.4	37.7

* Very finely ground up sample and then passed through 60 mesh sieves.

soil parent material,comprises the main factor influencing P sorption capacity of such soils. The more aluminous and less crystalline soils are,the more P is sorbed(Juo and Fox,1977). On the other hand,little is known concerning P sorption capacities of paddy soils under aerobic or anaerobic conditions. The material which follows relates several important properties of paddy soils to their P sorption capacity. These soil properties are: P sorption capacities under aerobic and anaerobic conditions, P extractable with Olsen's reagent,organic matter content, sodium dithionite extractable iron, iron in aqueous solution after anaerobic equilibration, pH of solution following anaerobic equilibration,and pH of soil paste. The data of these analyses of 46 paddy soils collected from 8 countries are presented in Table 5.

In general at low levels of added P, less P was sorbed under anaerobic conditions than under aerobic conditions. The reverse is true at high levels of added P(as in sample No. 37 of Fig. 6). In a few cases P sorption capacity of soils under anaerobic conditions was either consistantly greater (as in sample No. 44 of Fig. 6) or consistantly less (as in sample No. 38 of Fig. 6) than under aerobic conditions. Khalid et al.,(1977) reported similar results from experiments conducted in Louisiana.

Under aerobic conditions,the amounts of P required to establish 0.2 ppm P in solution increased linearly with increasing free iron contentin the soils(Fig. 7). A similar relationship was obtained between anaerobic P sorbed at 0.2 ppm

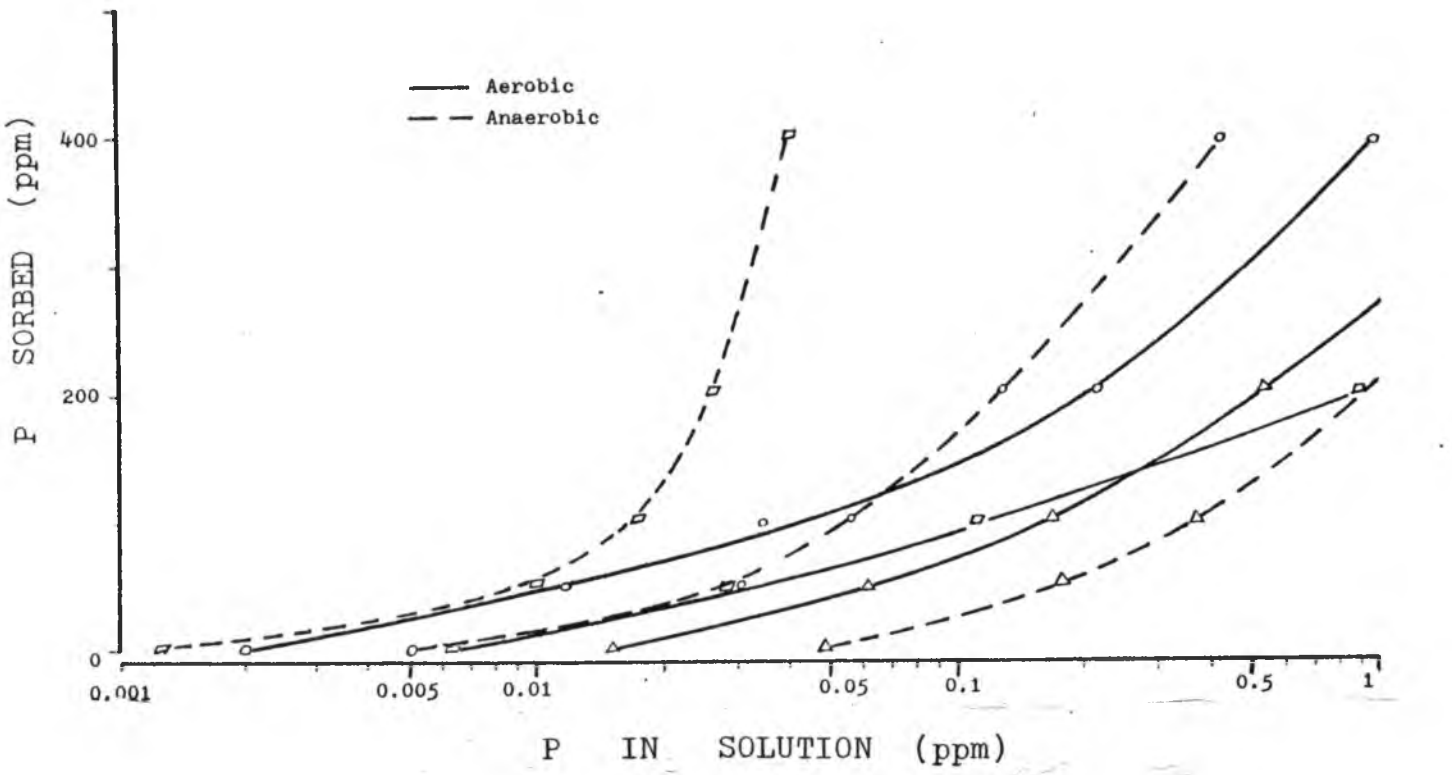

Fig. 6: Phosphorus sorption curves under aerobic and anaerobic conditions. Soil samples No. 37 (●), 38 (▲), 44 (◆).

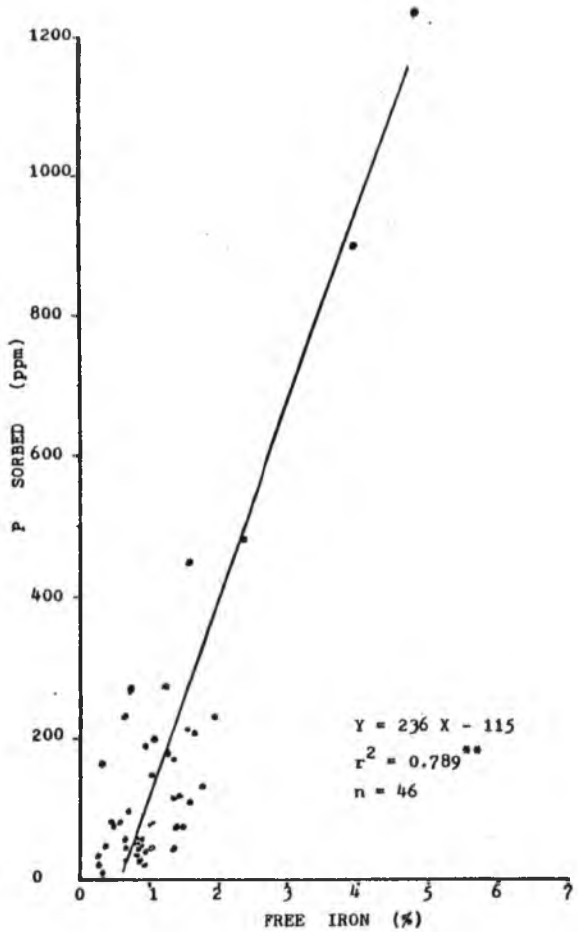

Fig. 7: Relationship between P sorbed (aerobic) at 0.2 ppm P in solution and free iron content of paddy soils.

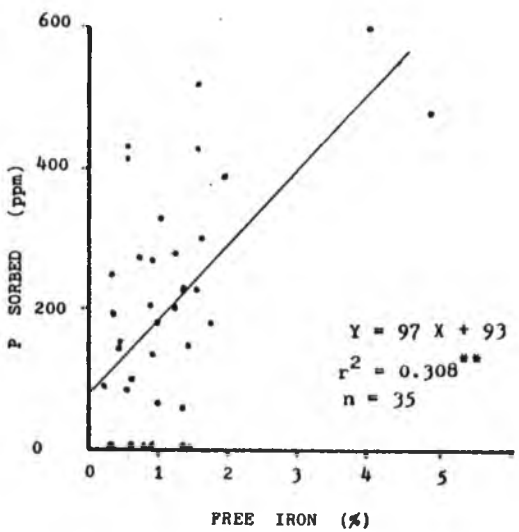

Fig. 8: Relationship between P sorbed(anaerobic) at 0.2 ppm P in solution and free iron content of paddy soils.

and free iron content in the soils (Fig. 8). Other soil properties measured in this study were not related to the P sorbed at 0.2 ppm in solution under aerobic or anaerobic conditions.

There was a tendency for soil pH to shift towards neutrality when soils were anaerobically equilibrated. The change was less than one pH unit. Ponnamperuma (1972) obtained similar effect of flooding under field conditions. Thus,anaerobic equilibration in the laboratory produces results similar to those obtained in the field.

Native soil organic matter did not influence the pH changes brought about by anaerobic incubation. However,the energy provided by the addition of 0.3%(soil dry weigh basis) rice straw to speed up the reduction process may have had an overriding effect on the native organic matter contents of the soils.

No relationship existed between the percentage of free iron in soils and iron solubilized during anaerobic equilibration.

Soil Test Values and Yield of Rice in Greenhouse Studies

A greenhouse experiment was conducted to investigate the use of P sorption curves for predicting the response of rice to applied P fertilizer. Four Hawaii soils having different P sorption capacities were used to grow rice to maturity. The amounts of P fertilizer applied to each

treatment,as indicated in Table 2,were based on the P sorption capacity of each soil in question and the concentration of native P in soil solution extracted from the reduced zone of the pots. The amount of P applied was generally small due to the attempts made to establish 0.1 ppm P as a center point of intended P in soil solution among treatments. Such a small amount of P applied is consistant with the amount generally used in the fields. Mukerjee (1964) stated that standard P fertilizer application for rice was 8.7 ppm (40 kg of P_2O_5 per hectare). Based on the slope of the P sorption curves which were developed under aerobic conditions(Fig. 2), with the possible exception of Lualualei soil, the amount of P applied did not appreciably change P in solution (Table 2). When comparing two soil test methods for P, one where soil was equilibrated with P solution under aerobic conditions and the other where the equilibration was under anaerobic conditions, the latter was less sensitive than the former. This was demonstrated by the steeper slope of the P sorption curves developed under anaerobic conditions than those developed under aerobic conditions.

In the case of Hanalei I, the anaerobic P sorption curve was positioned to the right of its aerobic P sorption curve. In the case of the other 3 soils(Hanalei II,Kaloko, and Lualualei soils), the aerobic and anaerobic P sorption curves crossed each other,so that at a low level of P added, the anaerobic P sorption curves fell to the right of the aerobic curves.

The effects of time and levels of P applied on water soluble P in the reduced zone of flooded soil materials in large pots are shown in Fig. 9 and Table 7. When no P was added the soil solution extracts of Hanalei I,Hanalei II,and Kaloko soils contained a higher concentration of P than the supernatant solution from the laboratory equilibrations. The results could be explained by higher soil to solution ratio in the flooded pots than in small tubes. It is interesting to note that in the Lualualei soil,the concentration of P in the soil solution extract of the reduced zone of flooded soil in pots when no P was added was approximately the same as in the supernatant solution of the anaerobic eqilibration in the laboratory.

At a given level of P applied, more P remained in the soil solution extracted from a pot than in the supernatant solution of a small tube after equilibration. However, the P concentrations in pots decreased for several weeks before reaching an equilibrium state (Fig. 9 and Table 7). The time required to reach equilibrium in the pots most likely was longer than in the laboratory,where samples were subjected to horizontal shaking. Gardner and Jones (1973) stated that equilibrium rates are sensitive to degree and frequency of mixing and also to temperature.

Two conclusions can be drawn from this study. First, if a small amount of P (8 ppm) was added to the soil,no detectable increase of P in solution could be measured following aerobic and anaerobic equilibrations. Secondly, P in

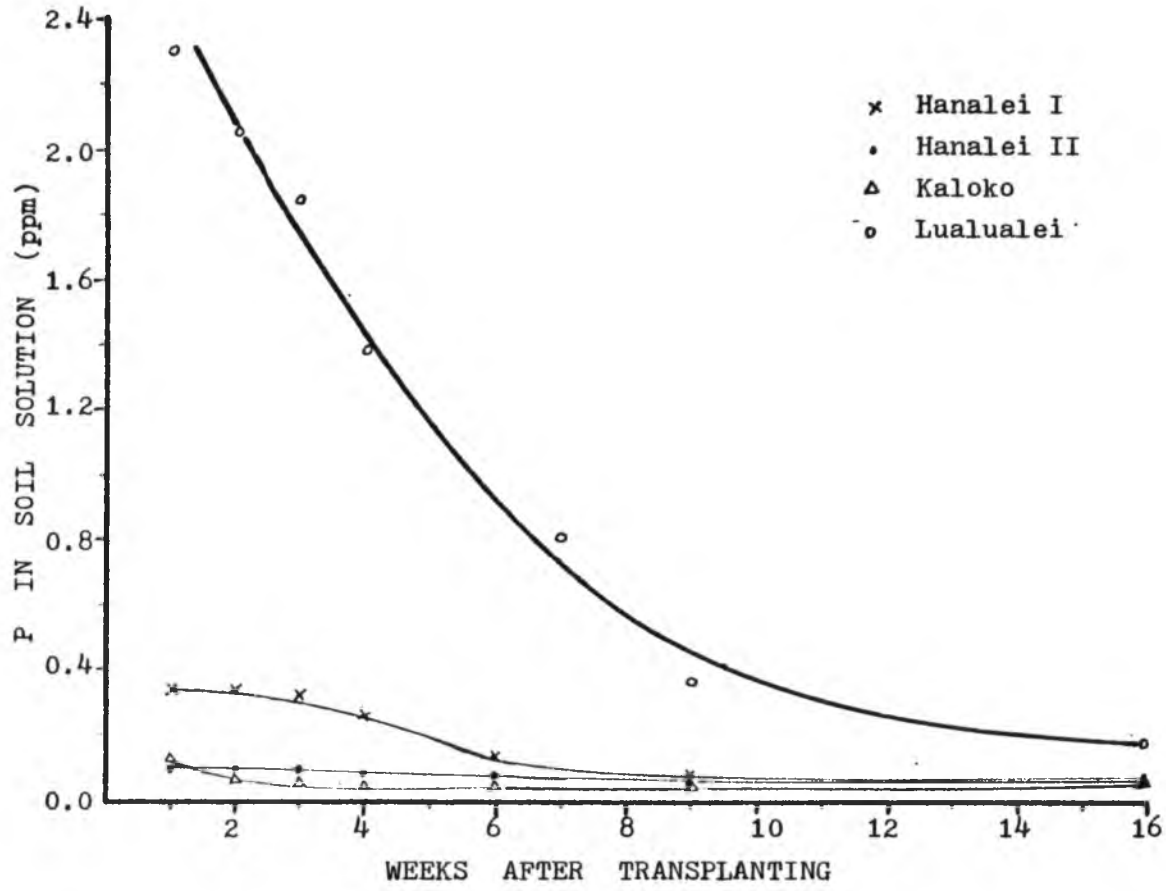

Fig. 9: Change with time in the average P concentration in soil solutions from the reduced zone.

Table 7: Phosphorus in soil solution extract of the reduced zone.

Soils	P treatments	Weeks after transplanting (ppm)							
		1	2	3	4	6	9	16	$\bar{X}$
Hanalei I	0	0.253	0.263	0.252	0.198	0.096	0.050	0.058	0.166
	1	0.240	0.283	0.312	0.239	0.117	0.123	0.078	0.199
	2	0.313	0.360	0.312	0.223	0.192	0.087	0.075	0.223
	3	0.570	0.490	0.442	0.354	0.184	0.077	0.078	0.314
	4	0.257	0.323	0.308	0.266	0.118	0.067	0.065	0.200
	$\bar{X}$	0.327	0.344	0.325	0.256	0.141	0.081	0.069	
Hanalei II	0	0.077	0.073	0.100	0.068	0.058	0.036	0.077	0.069
	1	0.153	0.100	0.119	0.109	0.058	0.071	0.070	0.097
	2	0.103	0.103	0.100	0.070	0.094	0.093	0.092	0.094
	3	0.180	0.085	0.106	0.118	0.164	0.073	0.145	0.124
	$\bar{X}$	0.110	0.090	0.106	0.091	0.094	0.068	0.096	
Kaloko	0	0.027	0.027	0.023	0.019	0.030	0.025	0.047	0.028
	1	0.037	0.047	0.029	0.018	0.035	0.026	0.066	0.037
	2	0.053	0.040	0.027	0.025	0.035	0.025	0.06	0.038
	3	0.110	0.047	0.039	0.028	0.032	0.019	0.040	0.045
	4	0.187	0.090	0.062	0.067	0.058	0.033	0.065	0.079
	5	0.333	0.177	0.135	0.096	0.083	0.168	0.086	0.154
	$\bar{X}$	0.124	0.071	0.053	0.042	0.040	0.049	0.061	
Lualualei	0	0.943	0.993	0.831	0.510	0.426	0.260	0.076	0.577
	1	2.113	2.007	1.825	1.491	0.795	0.193	0.081	1.215
	2	1.633	1.497	1.528	1.064	0.599	0.229	0.093	0.949
	3	2.073	1.897	1.891	1.318	0.743	0.325	0.160	1.191
	4	4.767	3.877	3.250	2.480	1.532	0.851	0.571	2.475
	$\bar{X}$	2.306	2.054	1.851	1.373	0.819	0.372	0.196	

solution in the reduced zone of flooded soil in pots increased more upon additions of small increments of P than occured in small tubes. Since a rice plant acquires most of its P in the early stages of growth, the high P concentration in the soil solution extract established at the beginning of the pot study would increase the yield of rice.

The yield of rice did not respond significantly to applied P in any of the four soils used in the greenhouse studies. Fig. 10 shows the relationship between relative maximum yield of rice and P in solution (aerobically equilibrated) for the pot study. The lowest concentrations of P were: 0.004 ppm (under aerobic equilibration), 0.006 ppm (under anaerobic equilibration), and 0.07 ppm (in soil solution extracted from the reduced zone). These equilibration results were inconsistant with previous findings. Katyal, (1978) reported that an average of 0.05 ppm P in soil solution extract was necessary to raise the P content of the rice plant above the critical level of 0.1%. Tanaka, (1962) and Hossner et al., (1973) reported 0.1 ppm of water soluble P was necessary to support normal growth of rice in solution culture and to achieve maximum growth of young rice in flooded soil.

Phosphorus supply in the four Hawaii soils used in the greenhouse studies was adequate to support normal rice grain production. The average grain yield of rice grown in Kaloko soil was about 50% as great as that from the Hanalei I, Hanalei II, and Lualualei soils (Table 8). Based on 25 cm X 25 cm spacings, the average yields were about 7.7 tons/ha in the

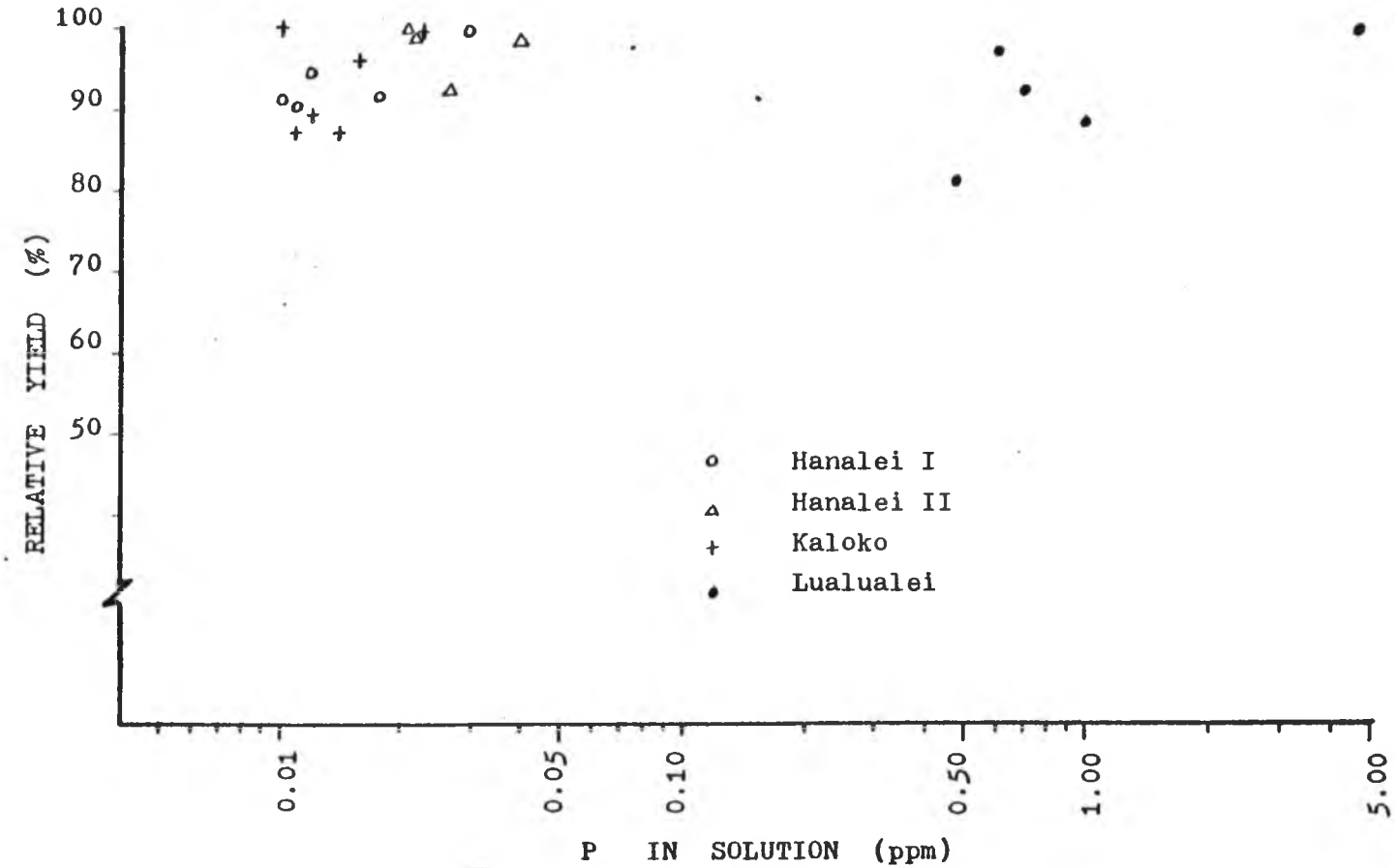

Fig. 10: Relationship between relative grain yield of rice and P in solution following aerobic equilibration.

Table 8: Yield of rice and Azolla.

Soils	P treatments	Rice yield					Azolla yield	
		Grain	Straw	Flag leaves	Grain	Straw	Drymatter (g)	P content (%)
		g			% P			
Hanlei I	0	108.5	89.0	0.249	0.296	0.072	0.13	0.106
	1	106.4	89.1	0.237	0.243	0.067	0.17	0.071
	2	111.6	84.9	0.225	0.330	0.075	0.29	0.100
	3	107.3	81.1	0.262	0.306	0.076	0.32	0.099
	4	118.2	94.4	0.229	0.280	0.076	0.27	0.108
Hanalei II	0	93.8	69.0	0.239	0.263	0.089	0.11	0.077
	1	93.0	74.6	0.235	0.278	0.087	0.13	0.087
	2	86.9	69.2	0.270	0.284	0.083	0.25	0.138
	3	92.0	67.4	0.258	0.276	0.096	0.13	0.092
Kaloko	0	52.6	54.7	0.175	0.255	0.052	----	-----
	1	46.3	43.2	0.184	0.280	0.064	----	-----
	2	47.2	43.0	0.189	0.342	0.085	----	-----
	3	46.0	34.6	0.189	0.260	0.073	----	-----
	4	51.0	43.4	0.197	0.268	0.070	----	-----
	5	47.3	43.5	0.224	0.271	0.090	----	-----
Lualualei	0	83.7	62.4	0.212	0.230	0.053	0.28	0.115
	1	99.9	83.1	0.227	0.271	0.052	0.45	0.184
	2	95.1	76.4	0.225	0.306	0.053	0.13	0.163
	3	91.0	77.1	0.228	0.294	0.058	0.56	0.152
	4	103.1	81.1	0.238	0.328	0.068	0.74	0.142

Kaloko soil,and about 15.4 tons/ha in the rest of the soils. These high yield figures do not apply directly to field contions of course, but indicate that normal growth of rice was obtained in the greenhouse.

Analyses of the second fully expanded leaves at panicle initiation showed no evidence of nutritional deficiency (Table 9). Phosphorus content in flag leaves ranged from 0.225% to 0.262% in the Hanalei I soil, from 0.235% to 0.270% in the Hanalei II soil, From 0.175% to 0.224% in the Kaloko soil, and from 0.212% to 0.238% in the Lualualei soil(Table 8). The critical P content in leaves is 0.1% (Tanaka and Yoshida, 1970). In the Kaloko soil where the lowest native P was determined,P content in leaves increased with increasing P concentration in soil solution extracts.

Phosphorus Experiments on Rice in the Field

To estimate the external P requirement of rice grown in the field,soil samples from control plots where no P was added, together with yield data, were obtained from cooperaters in several countries. Among the 40 experiments, 30 were conducted in Taiwan by the Taiwan Agricultural Research Institute. The levels of phosphate fertilizer applied were 0, 36, and 72 kg of P_2O_5 per hectare. The other 10 experiments were conducted in 5 different countries (4 in Thailand, 2 in Bangladesh, 2 in India, 1 in Indonesia, and 1 in Sri Lanka) under the project name of International Network on Fertilizer Efficiency in Rice (INFER) which was co-sponsored by the

Table 9: Nutrients content of 2nd. fully developed rice leaves at panicle initiation.

Elements	Soils				Critical content[1]		
	Hanalei I	Hanalei II	Kaloko	Lualualei	Critical content	Plant part analyzed	Growth stage[2]
N	3.48%	2.15%	2.43%	2.64%	2.5%	Leaves	Mat.
P	0.25%	0.23%	0.21%	0.20%	0.1%	Leaves	Til.
K	1.10%	0.80%	0.93%	1.24%	1.0%	Leaves	Til.
Ca	0.34%	0.34%	0.38%	0.34%	0.15%	Straw	Mat.
Mg	0.26%	0.25%	0.19%	0.14%	0.1%	Straw	Mat.
S	0.22%	0.24%	0.21%	0.14%	0.1%	Straw	Mat.
Fe	87.5 ppm	85.0 ppm	40.0 ppm	40.0 ppm	70 ppm	Leaves	Til.
Zn	13.8 ppm	13.3 ppm	16.5 ppm	13.5 ppm	10 ppm	Shoot	Til.
Mn	40.0 ppm	274.0 ppm	155.0 ppm	175.0 ppm	20 ppm	Shoot	Til.

1 Data extracted from "Nutritional Disorders of the Rice Plant in Asia." by Tanaka,A and S. Yoshida, 1970.

2 Mat. - maturity ; Til - tillering.

International Rice Research Institute (IRRI) and the International Fertilizer Development Center (IFDC). The levels of superphosphate for the 10 experiments were 0, 20, 40, and 60 kg of P_2O_5 per hectare. Only in 5 of the 40 experiments did yield respond significantly to P applied. Among these, 2 were from Bangladesh, 2 from Thailand, and 1 from India.

Figures 11 and 12 show that most soils contained adequate P for normal rice production, as indicated by a high proportion of points above the 90% of maximum yield level. The aerobic and anaerobic P sorption curves show that the external P requirement (P in solution required to produce 90% of maximum yield) was about 0.003 ppm. This is a very low value, and cannot be determined without considerable uncertainty. Fox,(1979) indicated that typical P concentrations in bulk soil solutions of productive upland soils were in the range of 0.01 to 0.1 ppm.

Yield response of rice (where there was one) to a small increment of P applied was dramatic. In soil No. 37,a soil from Thailand,an addition of 4 ppm P (dry weight basis) was enough to raise the yield from 53% to 97% of maximum. Fig. 11 indicates that 6 ppm of extractable P (Olsen's method) was sufficient for at least 85% of maximum grain yield. Grain yield data were not plotted against soil P concentrations obtained under anaerobic condition because P sorption curves under anaerobic conditions were difficult to reproduce in some soils.

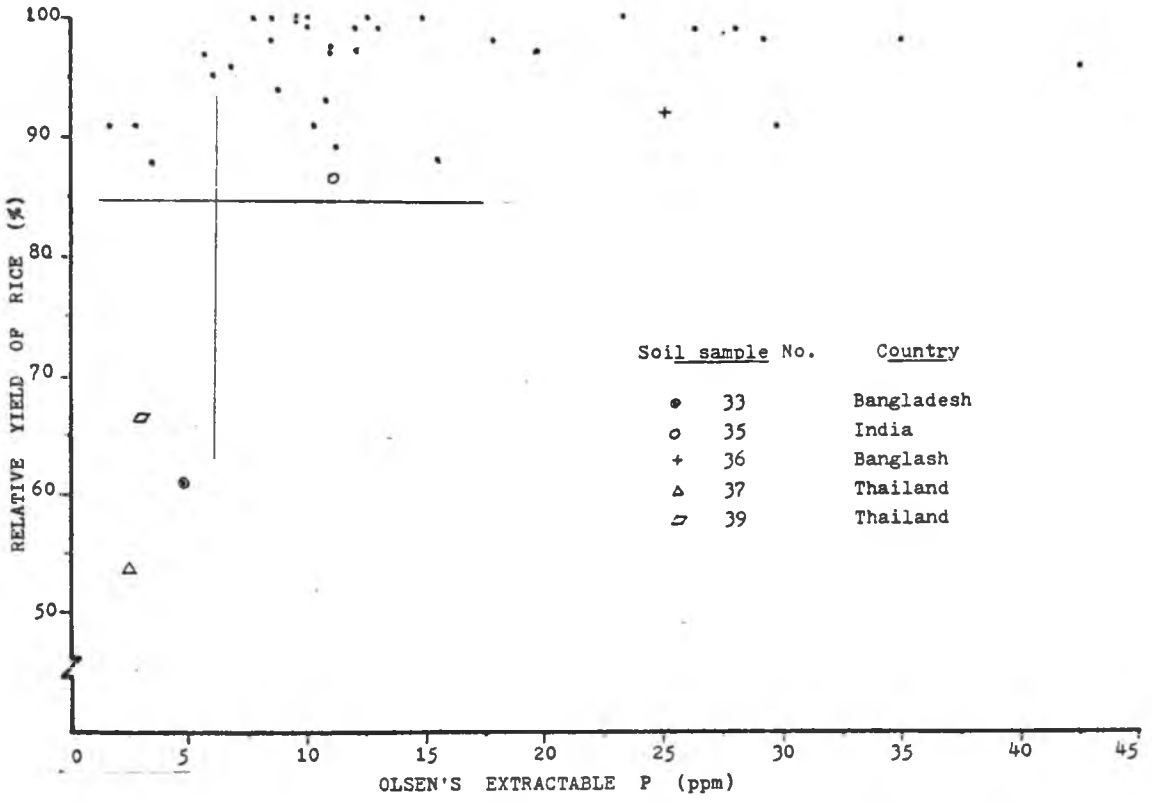

Fig. 11: Relationship between relative grain yield of rice and extractable soil P.
(.) : a soil giving no yield response to applied P.

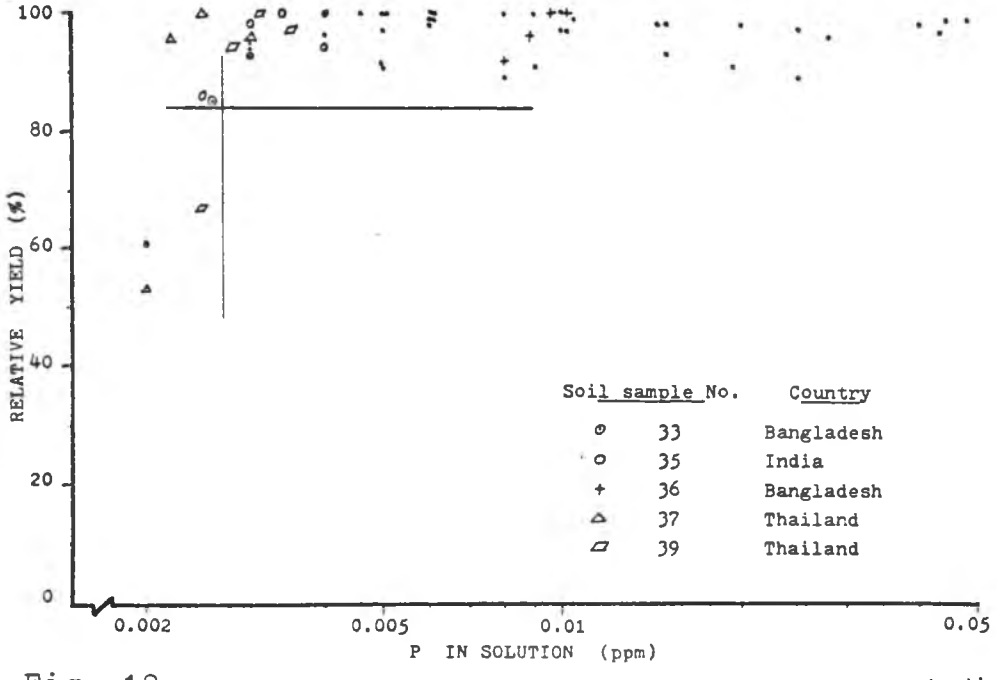

Fig. 12: Relationship between relative grain yield of rice and P concentration in solution (aerobic). (.) : a soil giving no yield response to applied P.

The roots of the rice plant must be very efficient in absorbing P from flooded soils. Only 4 ppm added P was required to achieve 90% of maximum yield in soils which were P deficient. Soil tests are insensitive to small changes in P status of soils as would be occasioned by such a small application of P. Most of the paddy soils studied were not P deficient. Small amount of P required can be effectively applied by dipping the roots of the rice seedlings in a P solution before transplanting, and such a procedure has been developed. The standard procedure involves dipping rice seedling roots prior to planting in super-phosphate-soil-slurry (Katyal et al.,1975). Later work indicated that 16 kg/ha of P_2O_5 applied to roots as a P-soil-slurry improved grain yield as effectively as 30 kg/ha of P_2O_5 applied by conventional method (Katyal, 1978).

Phosphorus in Solution and Yield of Azolla

Azolla is an aquatic fern which floats on water surface with its roots hanging down toward the soil surface. Phosphorus deficiency severely affects the growth of Azolla and its nitrogen accumulation (Watanabe et al.,1977). Little is known of the P requirement and the mechanism of P supply to Azolla. In a greenhouse experiment an attempt was made to study the effect of P applied to the soil on the growth of Azolla which floats on the water surface.

Among the four Hawaii soils used in pot studies,3 soils (Hanalei I, Hanalei II, and Lualualei) had adequate P to support the growth of Azolla, while Kaloko soil did not.

Azolla dry matter production increased with increasing P content in the plant material (Fig.13). The highest P content of Azolla was 0.184%. In a separate study,where there was vigorous growth of Azolla in culture solution containing 1 ppm P, phosphorus content of the plant material was 0.21% .

Phosphorus applied to the soil was assumed to diffuse to the free surface solution flooding the soil (Fig. 1). Concentrations of P in the free surface solutions increased with increasing amount of P applied (Table 2). A highly significant linear correlation (r^2 = 0.844**) was obtained between P in free surface solution and P in soil solution extract of the reduced zone determined 3 weeks before the introduction of Azolla.

Before the introduction of Azolla , it is reasonable to assume that P determined in the free surface solution was in equilibrium with P in the soil solution extracted from the reduced zone (which in turn was in equilibrium with P in the solid phase). Three weeks after the introduction of Azolla into the pots, P in the free surface solution was so low it could not be detected. Thus, the immediate source of P for Azolla was the P in solution, bathing its roots, and probably its fronds also. However Azolla continued to grow, still responding to the amount of P applied to the soils. Thus, there must have been a continous supply of P from the reduced zone to the Azolla by diffusion of P from the soil solution in the reduced zone to the oxidized layer and finally to the free surface solution (assuming that Azolla roots were not in con-

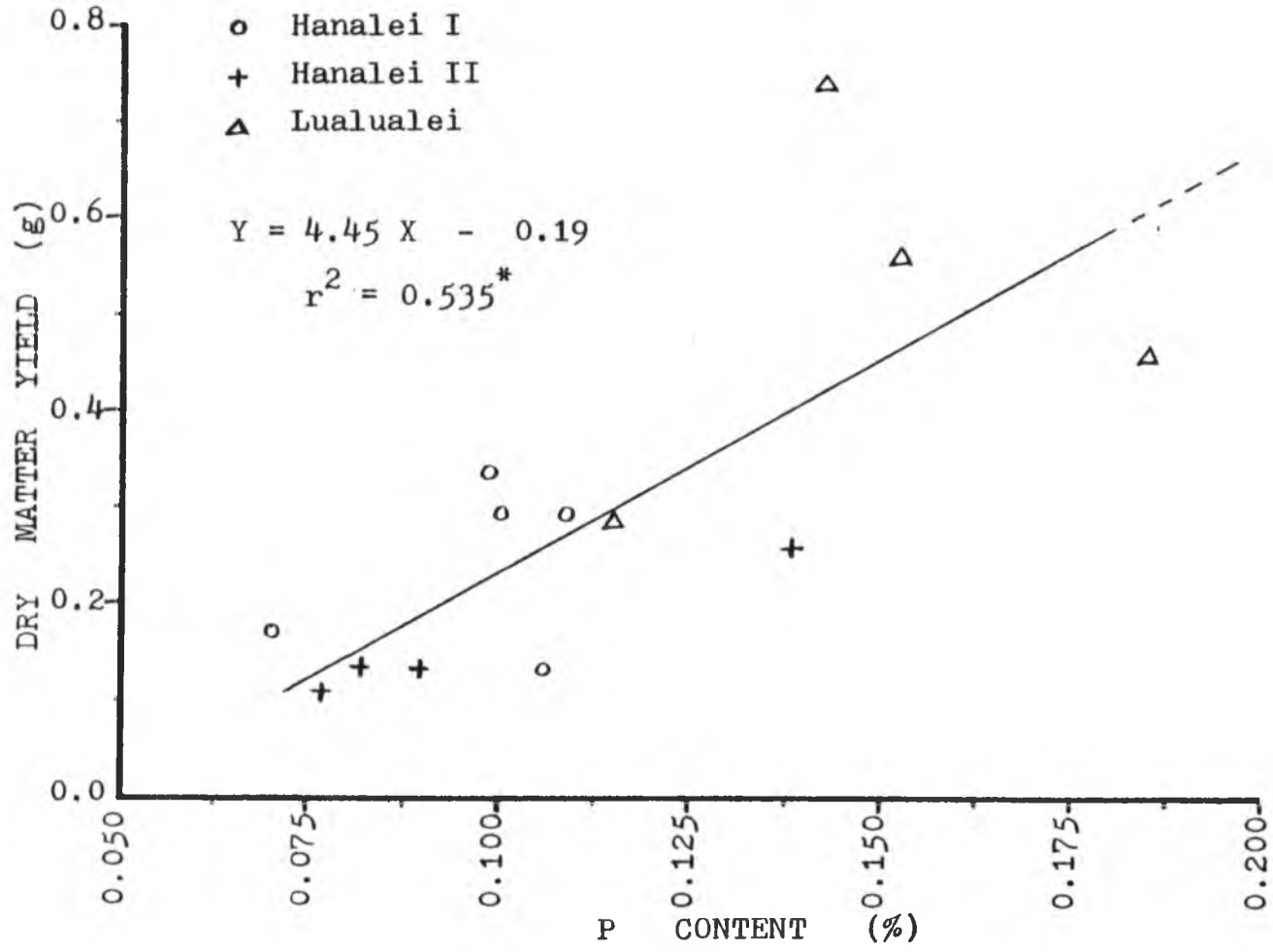

Fig. 13: Relationship between yield of Azolla and its P content.

tact with the soil surface). With certain assumptions Fick's law of diffusion can be used to estimate the amount of P diffused to the free surface solution during the seven week-period of Azolla growth.

Fick's law is: $F = -DA(d_c / d_x)$

where F is the amount of solute diffused per unit time; D is the diffusion coefficient of solute in the free surface solution; A is the surface area to diffuse through; and d_c / d_x is the concentration gradient of the solute. In applying Fick's law the following assumptions were made:

a) free surface water flooding the soil contained no colloidal suspension, implying that the tortuosity factor is unity and the diffusion coefficient of P was 1.07×10^{-3} cm^2/sec.

b) the surface area of diffusion was the soil surface area: $4.5cm \times 4.5cm \times 3.14 = 63.71cm^2$

c) the concentration gradient was the difference per unit distance between the equilibrated P in solution at the soil surface and the concentration of P at the root surface. Phosphorus determined in free surface solution before the introduction of Azolla was considered to be the concentration of equilibrated P at the surface of the soil throughout the growth period. Phosphorus determined in free surface solution three weeks after the introduction of Azolla was considered to be P concentration near the root surface. Using an

average depth of free surface solution of 4 cm, the P concentration gradient was calculated using the following equation:

$$d_c/d_x = \frac{\text{P before Azolla intr.} - \text{P after Azolla intr.}}{4 \text{ cm}}.$$

Table 10 indicates that the amount of P estimated to have diffused into the free surface solution during a seven-week growth period was consistently greater than the total amount of P taken up by the Azolla. The fact that Azolla growth responded to applied P, and that P uptake by the plant was less than the estimated total P diffused, led to the conclusion that the equation overestimated the amount of P diffused from the reduced zone into the solution bathing the roots of Azolla. It is probable that in a system where P has to diffuse through an oxidized layer, the diffusion rate of P is less than was assumed here. The presence of a thin layer (usually much less than 1 cm thick) of oxidized soil material composed of reprecipitated Fe(III) and Mn(IV) at the surface may decrease the rate of P diffusion considerably. Through occasional rupturing of the oxidized layer, either by gas bubbles or by animals, P diffusion and movement in bulk can be enhanced. Further work is required to quantitatively study the effect of this oxidized layer on the diffusivity of P during paddy cultivation in those situations where Azolla is considered as a potential green manure crop.

After harvest, the oxidized and reduced zones in the

Table 10

A comparison between estimated diffused P and P uptake by *Azolla*.

Soils	P treatments	Estimated P diffused	P uptake by *Azolla*
		mg	
Hanalei I	0	1.88	0.14
	1	1.59	0.12
	2	2.09	0.29
	3	2.74	0.32
	4	2.02	0.29
Hanalei II	0	1.15	0.08
	1	1.75	0.11
	2	2.09	0.34
	3	5.63	0.12
Lualualei	0	3.03	0.32
	1	1.73	0.83
	2	3.90	0.21
	3	8.58	0.85
	4	81.89	1.05

pots were sampled and subjected to anaerobic P desorption. Phosphate in the equilibrated solution was 5 to 85 times more concentrated in the oxidized layer than in the soil material from the reduced zone (Table 11). Phosphate treatments which were originally applied to those pots were reflected in the concentration and the quantity of P desorbed from the oxidized layer, but they were not reflected in the concentration of P desorbed from soil material of the reduced zone. This led to the conclusion that the oxidized layer retained water soluble P at the expense of the reduced layer. The high P retention capacity of the oxidized layer therefore reduced the rate of P diffusion from the reduced zone to the free surface solution.

If Azolla is to be incorporated into a cropping system involving lowland rice,it may need to be considered as a crop in its own right. Since it floats on the water and yet obtains its nutrients from the soil with which its roots are usually not in contact,a new set of criteria will be needed for estimating the fertility status of the soils involved. Thus far,no data are available on the levels of soil P required to sustain the growth of Azolla.

There are highly significant logarithmic relationships between dry matter yields of Azolla and concentrations of P in soil solution extracts of the reduced zone and P desorbed from the oxidized layer of soil materials. These relationships are described by the following equations:

a) Azolla dry matter yield versus P concentration in the

Table 11: Phosphorus concentration in supernatant solution before the introduction of Azolla and anaerobically desorbed and extractable P after the harvest of rice and Azolla.

Soils	P treatment levels	P in Standing water	Anaerobically desorbed P		Extractable P[1]	
			Oxidized layer	Reduced layer	Oxidized layer	Reduced layer
		ppm				
Hanlei I	0	0.026	0.027	0.001	2.99	4.37
	1	0.022	0.051	0.002	7.46	6.50
	2	0.029	0.038	0.001	11.12	7.27
	3	0.038	0.073	0.002	16.85	10.50
	4	0.028	0.034	0.007	7.41	10.90
Hanalei II	0	0.021	0.031	0.017	18.50	22.99
	1	0.024	0.034	0.013	17.47	26.99
	2	0.029	0.027	0.014	21.71	23.68
	3	0.078	0.052	0.007	30.20	27.81
Kaloko	0	0.018	0.053	0.006	4.73	9.12
	1	0.015	0.041	0.006	2.66	9.63
	2	0.026	0.052	0.008	4.89	12.19
	3	0.018	0.065	0.006	4.84	11.64
	4	0.075	0.067	0.007	6.89	10.55
	5	1.444	0.566	0.007	14.79	13.23
Lualualei	0	0.042	0.192	0.033	5.47	6.45
	1	0.024	0.167	0.047	6.27	7.25
	2	0.054	0.155	0.042	6.85	7.60
	3	0.119	0.291	0.034	6.95	8.69
	4	1.135	0.459	0.078	18.82	11.70

1 Olsen et al. (1954).

soil solution extracted from the reduced zone at the time when Azolla was introduced.

$Y = 0.443 \log X + 0.710 \qquad r^2 = 0.773^{**}$ (Fig. 14)

b) Azolla dry matter yield versus the mean of two values of P concentration in the soil solution extracted from the reduced zone:first, at the time Azolla was introduced, and second, at the time of harvest.

$Y = 0.533 \log X + 0.807 \qquad r^2 = 0.773^{**}$ (Fig. 15)

c) Azolla dry matter yield versus anaerobically desorbed P from the oxidized layer.

$Y = 0.383 \log X + 0.738 \qquad r^2 = 0.751^{**}$ (Fig. 16)

d) Azolla dry matter yield versus P concentration in the supernatant solution determined before the introduction of Azolla.

$Y = 0.312 \log X + 0.176 \qquad r^2 = 0.621^{**}$ (Fig. 17)

Based on these correlation coefficients, P in soil solution extracted from the reduced zone and anaerobically desorbed P of the oxidized layer are suitable indices of P availability for Azolla. Anaerobically desorbed P of the oxidized layer alone should be a reliable availability index only insofar as it represents P diffusion from the reduced zone. In most cases anaerobically desorbed P in the oxidized zone represents P that was moved into a biologically inactive sink. Thus, the oxidized layer of the Kaloko soil anaerobically desorbed more P than the oxidized layers of the Hanalei I and Hanalei II soils, but the Kaloko soil did not have enough P to support the growth of Azolla. If Fe(III) is precipitated

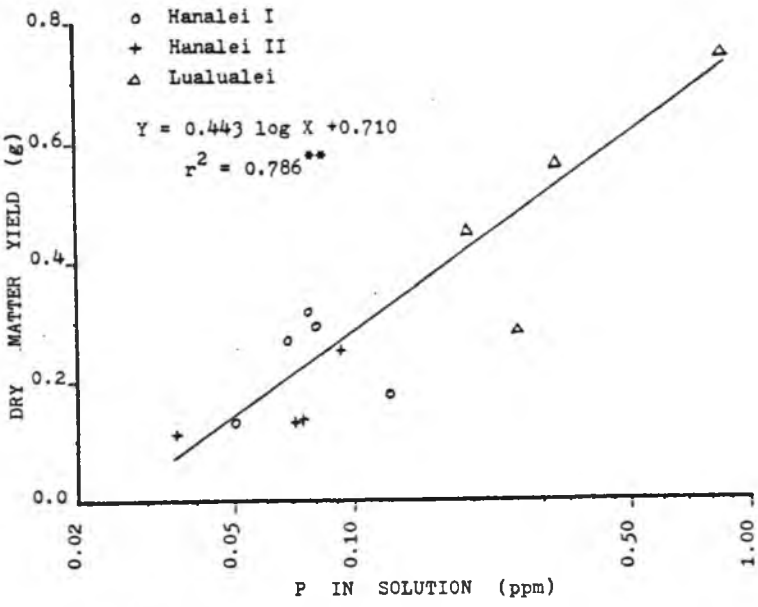

Fig. 14: Relationship between yield of Azolla and P concentration in soil solution determined at the time when Azolla was introduced.

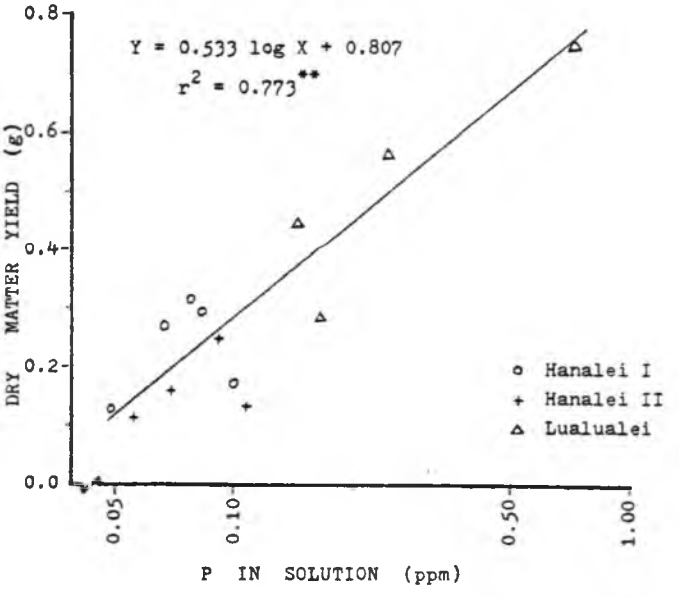

Fig. 15: Relationship between yield of Azolla and mean concentration of P in soil solution.

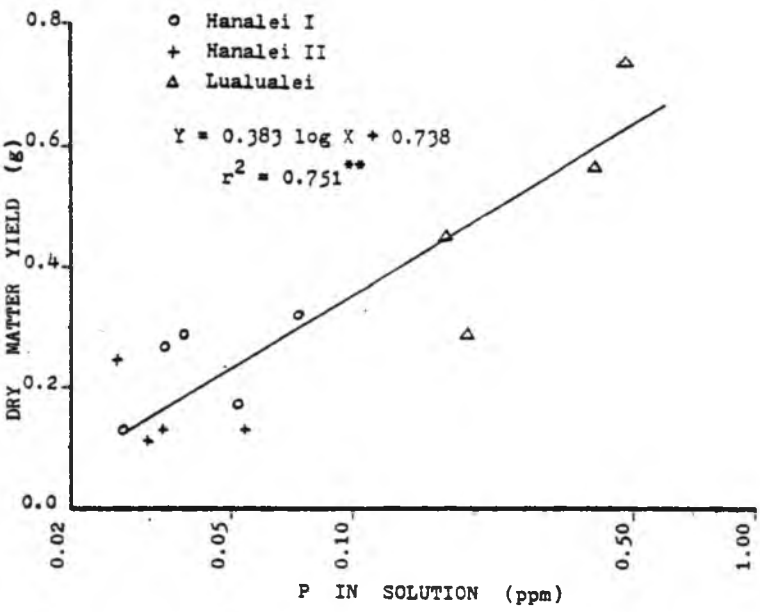

Fig. 16: Relationship between yield of Azolla and anaerobically desorbed P from the oxidized layer.

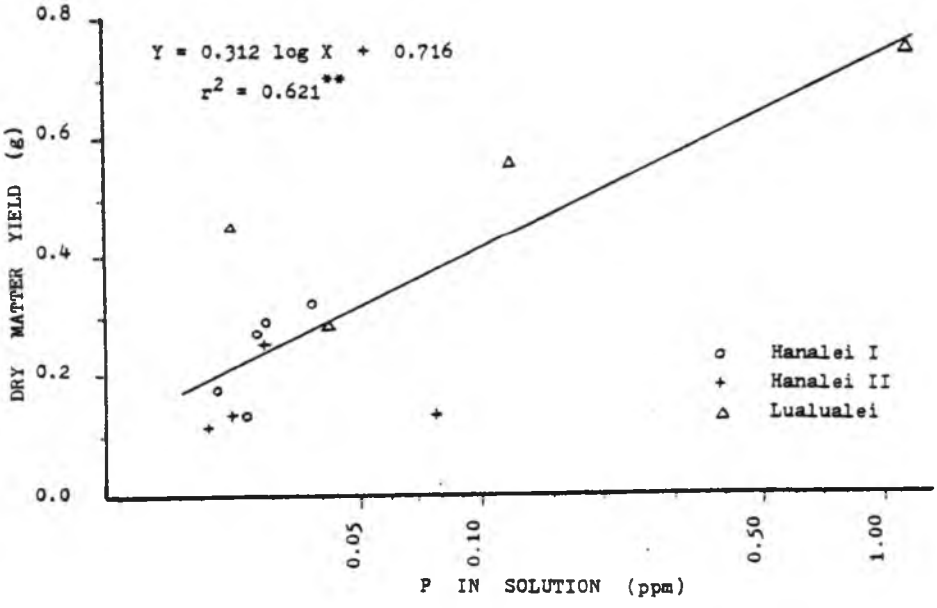

Fig. 17: Relationship between yield of Azolla and P in free surface solution (determined before introduction of Azolla.)

more rapidly in the oxidized layer than P can diffuse into it, a sink will be created, from which little P will be available to solution which bathes Azolla roots.

Summary and Conclusions

1) The mechanical difficulties in anaerobically equilibrating soil solution were at least partially resolved. However, difficulties were experienced in duplicating results of P analyses from some paddy soils. This leads to the question of applicability of evaluating the P requirements of soils using anaerobic P sorption curves.

2) Frequently, P sorption curves developed under anaerobic conditions crossed P sorption curves developed under aerobic conditions. The lower end of the anaerobic sorption curves is positioned to the right of the aerobic P sorption curves, resulting in steeper slopes.

3) The phosphorus of some Hawaii soils used in greenhouse studies was adequate for rice as indicated by a lack of yield response.

4) Phosphorus sorption curves (aerobic) appeared to be of some value in determining native P status of paddy soils. However, there is considerable uncertainty in determining P at such low concentrations.

5) Phosphorus sorption curves (aerobic and anaerobic) are not sensitive enough to detect changes in P status due to small additions of P fertilizer. Thus the use of P sorption curves for predicting P fertilizer requirements of

lowland rice cannot be recommended at this time.

6) Dry matter yield of Azolla increased with increasing P content of the plant, increasing P in soil solution, and increasing P desorbed from the oxidized layer of soil material.

7) Water soluble P is the main source of P supply for Azolla, and is diffused from soil in the reduced zone, directly or via the oxidized layer, to the free surface solution bathing the roots of Azolla. The calulated amount of P diffused from bulk soil to the solution bathing the roots of Azolla was about one order of magnitude greater than the amount of P taken up by Azolla.

8) External P requirement of Azolla is probably higher than that of the rice plant. None of the paddy soils studied are likely to have enough native P to support normal growth of Azolla. On the other hand a great majority of them have enough P to support normal growth of rice.

9) Additional studies are needed regarding the P management for Azolla production if Azolla is to be included in subsistence rice farming systems as a source of biologically fixed nitrogen.

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